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BACKGROUND

The Dry Deck Shelter (DDS) is a hyperbaric system used on submarines to transport SEAL delivery vehicles (SDVs) into an operating area. The system uses air from submarine banks to ventilate the DDS and provide breathing air to the divers. Because of the lack of carbon dioxide (CO₂) monitors, ventilation schedules are currently based on predictions to avoid exceeding the within-DDS CO₂ limit of 1.5% (15,000 ppm) surface equivalent (sev). These procedures result in high use of air bank gas and the need for frequent surfacing of the host submarine to ventilate the vessel prior to recharging the banks. High rates of bank recharging increases compressor workload and required preventive maintenance and repairs.

To improve efficiency of DDS ventilation, the Naval Medical Research Institute (NMRI) proposed development of a CO₂ monitoring system for use inside the DDS. This system would include portable CO₂ analyzers, modified for DDS conditions, which are carried into each of the 3 compartments of the DDS and mounted during operations. Ventilation could then be adjusted in response to changes in measured CO₂ levels within the DDS. This approach would minimize use of air bank gas during operations while insuring that ventilation is sufficient to avoid excessive CO₂. Where present procedures during operations overventilate the DDS, significant reduction in air consumption may be achieved.

The Naval Medical Research Institute as a result of the aforementioned proposal was tasked by the Naval Sea Systems Command ((NAVSEA (PMS-395)) in November 1995 to develop the proposed DDS monitoring system. As no reliable hyperbaric CO₂ analyzer was

available at the time, the task was directed toward development of an analyzer that would support DDS operations. This report describes this effort.

TASK OUTLINE

The task involving analyzer development and evaluation is outlined below:

1. Define requirements of analyzer.
2. Select commercially available candidate analyzer(s).
3. Modify candidate analyzer(s) to meet requirements.
4. Test prototype analyzers in laboratory and modify further where necessary.
5. Test final version of analyzer in laboratory.
6. Field test final version of analyzer during DDS operations.
7. Make recommendation regarding use of analyzer for DDS operations to NAVSEA.
8. Provide analyzer mounting and sampling information to DDS Planning Yard; provide operating and maintenance procedures to Fleet.

ANALYZER DEVELOPMENT

Analyzer requirements

Requirements for the DDS analyzer are defined below. Some of the requirements were defined prior to selection of the candidate analyzer; other requirements were added during the testing and development process and following additional discussions with NAVSEA and other Fleet personnel.

1. Essential

- a. Measurement range: < 1000 ppm up to 25,000 ppm (< 0.1% up to 2.5%) sev.

This measurement range brackets the current 15,000 ppm (1.5%) sev limit within the DDS. The low end of the range would also allow the analyzer to be used to screen air bank gas for CO₂ prior to DDS use, a requirement now met using less than optimal procedures. The current air bank limit is 1,250 ppm; revised procedures (1), developed by NMRI and undergoing field testing now, lower the limit to 1,000 ppm.

- b. Pressure range: 1 to 6 atmospheres absolute (ATA).

This meets the pressure range of DDS compartments during operations.

- c. Hyperbaric chamber safe.

Analyzer must be able to be operated safely (i.e., not inducing fires or explosions) inside a hyperbaric chamber exposed to high pressure O₂ mixtures. Offgassing of volatile contaminants must be below acceptable U.S. Navy limits for diving systems.

- d. Ambient temperature range: 10 to 35 °C.

This range is expected to bracket the DDS operational temperature range.

- e. Water resistant.

Analyzer will be exposed to high humidity and probably have some water contact (including potential dropping into the water) during DDS floodups. Some protection against failure under these conditions should exist.

- f. Usable in low-light conditions.

Analyzer must be easily operated and measurements accurately taken in the dimly lit DDS.

- g. Humidity: dry to ~90-100%.

The high humidity requirement reflects the conditions inside the DDS as given in item e.

- h. Powered by rechargeable battery, continuous analyzer operation without recharging > 8 h.

Analyzer batteries are expected to be checked and recharged, if necessary, immediately prior to DDS operations. Analyzers will be removed from the charger and installed in DDS compartments where they will be operated on battery power. Required 8-hour analyzer operation without recharging should insure sufficient battery life during all DDS operations.

2. Desired, but non-essential

- a. Remote readouts.

These would allow transmission of within-DDS CO₂ readings to a remote readout (digital display) inside the submarine for viewing by the dive supervisor.

- b. Short-term repeatability (within 10 min): $\pm 5\%$ relative over measurement and pressure range.

This level of precision should be easily met by a well-designed analyzer.

- c. Short-term accuracy (within 24 h of calibration): $\pm 10\%$ relative over measurement and pressure range.

Less accuracy (up to $\pm 20\%$) over the range of operating conditions would be acceptable if $\pm 10\%$ cannot be met and has been deemed satisfactory for DDS use (2). This degree of deviation from either the 15,000 ppm (1.5%) sev DDS limit or the proposed 1,000 ppm limit of air bank gas should not affect diver safety or performance. Analyzers are not expected to be used for more than 24 h before being recalibrated.

d. Calibration: 1 point span @ $\sim 15,000$ ppm ($\sim 1.5\%$) CO_2 /balance air;

Calibration using a CO_2 standard approximately equal to the value of interest (i.e., 15,000 ppm limit) should maximize accuracy at this concentration. In practical terms, the 15,000 ppm calibration point was also chosen because it is within the concentration range (12,000-15,000 ppm or 1.2-1.5%) of CO_2 in the calibration gas used for the shipboard mass spectrometer (CAMS) on all U.S. Navy nuclear submarines. Thus, the CAMS calibration gas could be used as a backup if the normal CO_2 calibration gas runs out. Tests done at NMRI will also indicate whether the analyzer will need to be recalibrated using a second, lower CO_2 standard to accurately screen the air bank gas for the proposed 1,000 ppm limit.

e. Response time: less than 60 s to 95% of reading.

f. Physical dimensions: volume less than 0.5 cubic foot.

Selection of candidate analyzer

Two candidate analyzers were selected based on a previous in-depth review and evaluation by NMRI of CO_2 analyzers for use at ambient pressures on U.S. submarines (3). Selection was based on factors including accuracy, measurement range, and ease of use. The 2

analyzers believed to show the most promise for successful modification for hyperbaric use inside a DDS are listed below:

1. Model CDM-1000/long; Geotechnical Instruments, Inc.; Leamington Spa, England.
2. Model RIKEN RI-411A; RKI Instruments, Inc.; Hayward, CA.

The two manufacturers were contacted by NMRI to determine their interest in the DDS project. Following a number of conversations, RKI Instruments did not appear interested in participating. Geotechnical Instruments, however, indicated that it would help us develop the hyperbaric analyzer. Thus, the Geotechnical analyzer was chosen as the initial unit for modification and evaluation for DDS use. It would have been preferable to have a second analyzer undergoing parallel development in the event that one candidate failed to meet the requirements. However, NMRI decided to proceed with the experiments. Another analyzer would be selected later if required.

The Geotechnical analyzer uses non-dispersive infrared detection as its method of analysis. Its measurement range is from 0 - 7.5% CO₂, with readings automatically compensated for barometric pressure and temperature and displayed on a digital readout. The analyzer is calibrated by introducing a span gas and adjusting the reading; no zero adjustment is required. A small internal pump draws sample gas (~500 ml/min at 1 ATA) into the analyzer where it passes through an optic bench with infrared source, filter, and detector. Analyzer is operated via the keypad in response to screen prompts. Other properties are listed below:

- i. Dimensions: 9 x 9 x 2 in
- ii. Weight: ~5 lb.
- iii. Power supply: internal rechargeable NiCad batteries 2 x 3.6 volt, 8-10 h of normal operations
- iv. Temperature range: 0 - 40 °C

Modifications of candidate analyzer

A number of modifications to the off-the-shelf non-hyperbaric Geotechnical unit were initially made by the manufacturer to meet our requirements (discussed earlier). Results from subsequent testing of first and later generation analyzers were used to define additional modifications that were then completed. The end product was the final generation analyzer that includes the following modifications:

1. Inlet redesigned

The humidity/temperature sensor on the inlet port of the original analyzer was found to leak sample gas into the instrument case. Because the sensor was not needed, it was removed and the inlet reconfigured to contain a Teflon filter for water protection (discussed below).

2. New keypad to withstand pressure

The original keypad was actuated by pressure, causing the instrument to shut off during compression. A tactile keypad was installed that would be unaffected by pressure.

3. Pressure equalization vents

A case vent (open bulkhead fitting) was installed on the side of the analyzer case to allow pressure equalization between the inside of the analyzer and outside pressure during compression or decompression. A second vent was installed to vent the battery compartment to the inside of the analyzer.

4. Electronic board coating

All electronic boards were conforma coated to protect against moisture and improve ruggedness.

5. Backlight

A low-voltage backlight was added to allow the digital display to be easily read in the DDS.

6. Brushless pump motor

The original sample pump incorporated a standard motor with brushes that could cause electric arcing. This pump was, therefore, unacceptable for use inside a hyperbaric chamber due to potential for fire and was replaced by a pump with a brushless motor. The new pump, like the original one, draws ~500 ml/min (at 1 ATA) of sample gas into the analyzer.

7. 10 ATA infrared detector

Although the original detector was not specifically designed for high pressures, this component tolerated pressure up to 6 ATA during preliminary testing. In order to increase ruggedness, the manufacturer replaced the detector with one rated up to 10 ATA.

8. Optic cell modifications

The optic bench (infrared cell) was modified to improve accuracy at pressure.

9. Pressure compensation to read up to 25,000 ppm (2.5%) CO₂ sev

A pressure transducer rated up to 10 ATA was installed and new software was developed to allow the analyzer to compensate for pressures up to 6 ATA and display CO₂ concentrations up to 25,000 ppm sev in ppm units.

10. Pressure reading displayed

Pressure (in fsw) measured by the transducer inside the analyzer is now shown on the display as an aid to the DDS operators.

11. Remote readouts and wiring

A remote repeater module was provided by the manufacturer so that the CO₂ concentration measured by the analyzer inside the DDS could be displayed on the host submarine. This would allow diving personnel on the submarine to control ventilation based on CO₂ levels. The display module operates from a 12-volt DC power supply that is powered by line current. The RS485 communications line is a 3-lead wire that can drive the repeater up to 1000 m away.

12. Water protection

Modifications were made to protect the analyzer from the wet, humid conditions inside the DDS and if accidentally dropped into the water during operations. The original analyzer had a gasket sealing the 2 halves of the case that was very effective in preventing water entry, even if

submerged under several feet of water. However, the cover to the battery compartment on the outside of the case was not watertight. To correct this, it was sealed with silicone caulk at the factory. For added protection, a waterproof aluminized adhesive label was applied to the outside of the case covering the battery compartment. Teflon filters (PTFE, 0.2 μm) were installed at 3 locations to prevent entry of water and aqueous aerosols: on the gas inlet port on the outside of the case, on the case vent, and on the battery vent.

If the analyzer is dropped into the water, it will float. If the pump is operating, water can be drawn into the inlet filter located on one side of the case and flow will stop. A flow sensor inside the analyzer will then detect the absence of gas flow and turn the pump off within several seconds. To put the analyzer back into operation, the filter is first removed by unscrewing the retaining nut and gently pulling it out by the fingers. The filter then can be replaced or simply blown out by mouth or with a gentle flow of gas.

13. Calibration with ~15,000 ppm (~1.5%) CO₂

All analyzers are individually calibrated at the factory using a range of CO₂ concentrations at 1 - 6 ATA. Factory calibration and software were developed to optimize accuracy at the DDS limit of 15,000 ppm sev, assuming a one-point field calibration using 15,000 CO₂. Additional adjustments were made to improve measurement at the proposed air bank limit of 1,000 ppm CO₂.

14. Battery charging

After analyzers are stored for several months without use, the main NiCad batteries become discharged and need to be recharged before the instruments can be turned on and used. If analyzers are not recharged at this time, the small backup battery (which receives its charge directly from the main batteries) becomes discharged over another few months. Subsequently, the original analyzers cannot be turned on after recharging the main batteries. This is because the backup battery, which maintains microprocessor clock time, is needed for startup but recharges only very slowly over a number of days from the main batteries. After modification of the original charging circuit, the charging current now is directly delivered to both the main and backup batteries. This allows analyzers to be brought back to operation after 24 hours of recharging, regardless of the length of time since they were last operated.

15. Case color

The original analyzer case color was changed from red to blue in response to Fleet requirements.

16. Disable automatic shutoff

The original analyzer came from the manufacturer with an automatic shutoff function so that if no keys were pressed after ~30 min, the unit would automatically shut off to conserve the batteries. This option could be turned off by the operator using a "hidden key" function. As automatic shutoff was not desired for DDS use, the manufacturer changed the default setting so that all units procured came with the shutoff disabled.

Description of final analyzer

The final analyzer was designated as a new product line by the manufacturer: Geotechnical Instruments, Inc.; Anagas Hyperbaric Analyzer; model HB 1.1. The Geotechnical product number for the U.S. Navy version of their HB 1.1 is HB 1.1A. The HB 1.1A unit includes a 0-25,000 ppm analyzer, blue analyzer case, battery charger, blue carry case, battery case sealed with silicone rubber and aluminized adhesive label, 5 spare Teflon filters, and operating manual. This analyzer, like the model (CDM-1000) from which it was adapted, uses non-dispersive infrared detection as its method of analysis. Its measurement range is from 0 to 25,000 ppm sev (2.5% CO₂) at pressures up to 6 ATA. Readout is in ppm units to the nearest 20 ppm. Following a step change in CO₂ concentration, analyzer reading stabilizes after ~40 s. The display is backlit so it can be read under low- or no-light conditions. Gauge pressure is also displayed in units of feet of seawater (fsw). The analyzer can be operated with an optional remote readout and can be set to log the data into memory, which can then be downloaded.

The analyzer can be operated in wet, humid conditions at temperatures ranging from 0 - 40 °C. If dropped into water, the instrument will float. If water enters the gas inlet, it will be trapped in the inlet filter and the sampling pump will shut off. The analyzer can be restarted by removing the filter and replacing it or by blowing it out by mouth or gentle gas flow.

Analyzers are calibrated by presenting a span gas: no zero gas is used. The concentration of the calibration gas can be entered to the nearest 1 ppm. For DDS use, the analyzer is run off its self-contained NiCad batteries. Overnight charging provides ~12 h of usage. For applications

other than DDS, the analyzer can be used when it is attached to the charger that plugs into 110-volt line current. However, the instrument must have batteries in place to operate.

ANALYZER TESTING

Analyzers tested

This report describes testing and results from 19 analyzers (Table 1) containing all the final modifications except as noted:

1. Six analyzers acquired during 1995 and used for field testing during 1995-1997. These did not contain the changes to the battery charging system which were made late in the investigation.
2. Thirteen units acquired in 1997 as the first group of analyzers to be delivered to the Fleet.

Testing of earlier generation analyzers, which did not contain all the final modifications, will not be discussed in detail in this report.

Besides the charging systems, the main difference between the field test and Fleet units was that the field test units had been modified during the development process to produce the final generation analyzer. This process involved shipping each of the 6 field test analyzers back to the manufacturer in the United Kingdom a number of times to correct problems and to make modifications. The sealed analyzer case was often opened and some of the electrical and mechanical components removed and replaced. On the other hand, the Fleet units were

manufactured after the final generation analyzer had been defined and were initially delivered to NMRI containing all the final modifications.

Hyperbaric test system

A specially designed hyperbaric test system was set up to allow controlled delivery of test gases to multiple analyzers under pressure (Fig. 1). This system included a hyperbaric chamber (Bethlehem model 183160 HP, Bethlehem, PA) configured with a gas manifold system that could handle up to 7 different test gas standards, as well as a cylinder of CO₂-free air (i.e., zero air). A bleed-down valve was used to vent manifold pressure when switching from one standard to another.

Inside the chamber, up to 4 analyzers were connected to the gas delivery circuit to sample gas from a flowing stream (Fig. 1). The gas delivery valve outside the chamber was adjusted initially at the surface before experiments began, so that a small excess flow of ~500 ml/min registered on the flowmeter (rotameter) inside the hyperbaric chamber with all analyzers operating. This insured that the analyzers sampled only test gas, and not ambient air, and that only minimal back pressure (< 1 psi) was placed on the flow to the analyzer. A tracking regulator allowed a fixed pressure differential (in this case, 10 psi) to be set and maintained between the test gas delivered to the analyzers and the hyperbaric chamber. Once flow was set at the surface, this necessitated, at most, a minimal adjustment to maintain the ~500 ml/min rotameter flow reading as the chamber was compressed.

As rotameter calibration and analyzer sampling rate were both undoubtedly affected by chamber pressure, the flowmeter was used to confirm sufficient flow to the instruments rather than provide accurate measurement of flow. In order to insure that analyzer readings were not affected by the delivery flow, preliminary tests varied the delivery flow from less than 300 ml (rotameter) to highly audible rates that probably exceeded 20 l/min. No effect on analyzer readings was observed at pressures up to 6 ATA.

The chamber, rated well beyond the maximum test pressure of 6 ATA, was equipped with separate air supply and decompression circuits so that it could be compressed with air or decompressed at precise rates. The travel rate for testing in this study was 1 fsw/s during compression and ~2 fsw/s during decompression. For analyzer testing, chamber pressure was monitored from a Heise pressure gauge (Dresser Industries Instrument Division, Newtown, CT) readable to the nearest 0.5 fsw. This gauge had been calibrated with a pressure comparator certified with pressure standards traceable to the National Institute of Standards and Technology (NIST). The temperature of the chamber was controlled from ~10 to 40 °C to within 1 °C of set point (Yellow Springs Instrument Co., Yellow Springs, OH). A humidifier was located outside the hyperbaric chamber and consisted of a stainless steel container of ~750 ml volume containing several 100 ml of distilled water. This could be switched into the circuit to bubble the test gas through the water column prior to delivery to the analyzers.

Laboratory testing

Instruments were stored, calibrated, and tested (other than hyperbaric exposures) at laboratory temperatures ranging between 19 and 24 °C. Occasionally, overnight storage temperatures were several degrees centigrade outside of this range due to problems with the building temperature control. Analyzers were recharged the night before each day's testing by connecting the battery charger, which was plugged into line power. The charger was disconnected the next day prior to calibration and testing so that all procedures were done with analyzers running on battery power.

The following gases were used during testing:

1. Zero air: CO₂-free, hydrocarbon-free air.
2. Seven gravimetric standards with the following nominal concentrations:

1,500 ppm (0.1500%) CO₂

2,500 ppm (0.2500%) CO₂

3,000 ppm (0.3000%) CO₂

3,750 ppm (0.3750%) CO₂

5,000 ppm (0.5000%) CO₂

7,500 ppm (0.7500%) CO₂

15,000 ppm (1.5000%) CO₂

25,000 ppm (2.5000%) CO₂

All of the above were in balance hydrocarbon-free air and obtained commercially and certified to $\pm 1\%$ relative.

Analyzers were tested in 2 locations in the laboratory: 1) on the laboratory counter at ambient pressure and 2) inside the hyperbaric chamber at pressures up to 6 ATA. In both cases, gas was delivered to one or more analyzers simultaneously via a branching circuit (Figs. 1-2) made of wide-bore (3/16 inch inner diameter) Tygon tubing and plastic tees so that a slight excess of gas exited the overflow. As discussed before, this insured that only test gas, not ambient air, was sampled. For countertop testing, overflow was adjusted to several liters/min; adjustment of flow inside the hyperbaric chamber was described above. As with the chamber testing, no effect on instrument reading was observed when gas flow to the instruments on the counter was varied over a wide range.

On the counter, gas was supplied to the analyzers via the branching circuit using a precision gas divider (STEC model SGD-710, Horiba Instruments, Inc., Ann Arbor, MI). The STEC device allowed blending of the CO₂ standards with a diluent gas (zero gas) in 10 equal steps from 0 to 100% of the standard CO₂ concentration. Teflon tubing was used to connect the standards and diluent gases to the STEC. This gas divider was previously shown to be linear to within the manufacturer's specification of $\pm 0.5\%$ of full scale, using low ppm levels of volatile organic compounds (4-5) and up to 25% of fixed gases (e.g., O₂, CO₂). With the STEC, an entire response curve could be generated from the 10 CO₂ concentrations from a single gas standard. A

water bubbler using a 500-ml flask filled with several inches of water could be put into the circuit downstream of the STEC to humidify the gas delivered to the analyzers.

Analyzers were turned on at the beginning of each test day, disconnected from the battery charger, and batteries verified as fully charged; analyzers were then allowed to warm up for at least 5 min. Analyzers were then calibrated together on the counter at ambient pressure, unless the protocol indicated otherwise. Calibration was done with a nominal 15,000 ppm (1.5%) CO₂ delivered by setting the STEC = 60 with the 25,000 ppm (2.5%) CO₂ standard connected. Laboratory barometric pressure in bars was measured using a digital barometer (model AG-200B; Sensotec, Inc., Columbus, OH), traceable to NIST, and used to calculate the percent CO₂ sev of the gas delivered from the gas standard to the analyzers:

$$\text{sev concentration (ppm CO}_2\text{)} = \text{standard concentration} *$$

$$(\text{STEC setting}/100) * \text{barometric pressure}/1000 * 0.98692$$

where the gas is delivered via the STEC device or

$$\text{sev concentration (ppm CO}_2\text{)} = \text{standard concentration} *$$

$$\text{barometric pressure}/1000 * 0.98692$$

where the gas is delivered directly. The factor, 0.98692, is used to convert bars to atmospheres. The sev concentration calculated in this manner was used for calibration and to define expected analyzer readings during testing.

Calibration involved checking each analyzer's digital readout in ppm against the sev concentration of the delivered CO₂ mixture. If the reading was not within 400 ppm of this value,

the analyzer was recalibrated by entering the correct concentration. Zero gas was then delivered to the analyzers and the reading recorded; no zero adjustment was possible. Calibration readings were taken after analyzers had stabilized, which typically took ~40 s following a gas switch.

Analyzer readings during actual testing were taken using the "ID" function for data storage. For testing on the laboratory counter, each data point was manually stored into instrument memory, after readings had stabilized, using the #6 "store" key. During testing inside the hyperbaric chamber, analyzers were put in the logging mode, which allowed automatic recording of data at set intervals. For this application, logging interval was set to 1 min and pump duration set to 60 s which made the sample pump run continuously and recorded one reading into instrument memory every 1 min. At the end of each test, data in memory was downloaded to a personal computer using UNICOM Analyzer Download Software, version 1.06 (Geotechnical Instruments, Inc.) and manipulated using spreadsheet software.

Analyzers were tested for the following:

1. Ambient pressure precision/accuracy

- a. Procedures. On the first day of this test, calibrated instruments were repeatedly presented with 15,000 ppm (1.5%) CO₂ (calibration gas) followed by zero gas. This was done 5 times over a 10-minute period and measurements recorded. Each analyzer was then recalibrated if the final reading was not within 400 ppm of the calibration gas. STEC response curves were then generated by varying the STEC setting from 0 to 100% and back to 0 using first the 25,000 ppm (2.5%) CO₂ standard and then the 2,500 ppm (0.25%) standard. Following this, STEC

curves were repeated by using humidified STEC gas. With humidified gas, the STEC was varied only from 0 to 100% using first the 2,500 ppm standard and then the 25,000 ppm standard. Testing with only increasing concentrations of CO₂ avoided problems resulting from the gas dissolving in the water of the humidifier and subsequently affecting the CO₂ level of gas delivered to the analyzers. Analyzers were then turned off. Total test time was 2-3 h. The second day, calibration of each analyzer was checked, but not readjusted, and zero gas measured prior to repeating the STEC tests as done the first day. Following this, analyzers were then recalibrated with 1,000 ppm CO₂ before repeating the STEC curve using only the 2,500 standard.

b. Test schedule. The first 6 field test units were tested weekly for 4 weeks to document performance in detail during the early evaluation period. The 13 Fleet units were tested for only 2 weeks to insure that each analyzer was operating satisfactorily prior to delivery to the Fleet. Humidified gas testing was done only with the 6 field test units; testing after calibration with 1,000 ppm CO₂ was done only with the 13 Fleet units.

c. Rationale. These tests defined precision and linearity of instruments at ambient pressure over ~24 h period, which should be longer than analyzers are used in the field without recalibration. The humidified tests examined whether water vapor significantly effected accuracy, which could be important in the DDS environment. Testing following recalibration with 1,000 ppm CO₂ evaluated the expected improvement in accuracy at low levels of CO₂. This would be important for the secondary requirement of screening air bank gas.

2. Hyperbaric accuracy

a. Procedures. On the first day of this test, calibrated instruments were put into the hyperbaric chamber, which was set at 21 °C (± 0.5 °C). Ten minutes was allowed for equilibration. Gas standards were then delivered to the analyzers at pressures up to 6 ATA, according to Table 2, which restricted testing up to 25,000 ppm (2.5%) CO₂ sev. Testing began with the lowest CO₂ standard at 1 ATA. Pressure was then increased in 1 ATA steps up to 6 ATA and then back to 1 ATA, waiting at each new pressure for 3 min for readings to stabilize before recording. Testing was repeated with the other standards in order of increasing CO₂ concentration and up to the maximum test pressures in Table 1. When all 7 standards had been tested, hyperbaric testing was repeated using humidified gas, but with only the 4 standards, 1,500, 3,000, 5,000, and 15,000 ppm CO₂ to reduce testing time. Again, to avoid CO₂ buildup in the humidifier, testing was done only with increasing pressures from 1 to 6 ATA and not during the return to 1 ATA. Analyzers were then turned off. Total test time was 4 h.

The second day, calibration of each analyzer was checked, but not readjusted, and zero gas analyzed prior to repeating the hyperbaric testing as per the first day. When this testing was completed, the analyzers were reset to factory calibration by performing several keypad strokes and hyperbaric testing was again repeated. Analyzers were then turned off. Total test time was 6 h.

b. Test schedule. As with the ambient pressure testing, the first 6 field test units were tested weekly for 4 weeks and the 13 Fleet units for 2 weeks. Humidified gas testing was done

only with the 6 field test units; testing after re-setting analyzers to factory calibration was done only with the 13 Fleet units.

c. Rationale. These tests defined instrument performance at CO₂ concentrations and absolute pressures that span the range of operating exposures. As with ambient pressure testing, water vapor effects were evaluated and testing was done over ~24-hour period. Resetting to factory calibration was evaluated as an option in the field when normal calibration could not be done.

3. Effect of ambient temperature

a. Procedures. Calibrated instruments were put into the hyperbaric chamber, which was set at 21 °C. Ten minutes was allowed for equilibration. Hyperbaric testing was done as before but with only the 4 standards: 1,500; 3,000; 5,000; and 15,000 ppm CO₂. Testing was conducted during increasing chamber pressures in order to reduce testing time. Following surfacing from 6 ATA, the chamber temperature controller was adjusted to either maximum cooling (~10 °C), maximum heating (~40 °C), or left at 21 °C (control). After maximum temperature was reached (< 5 min), chamber temperature fluctuated no more than ± 1 °C. Two hours were allowed for analyzer equilibration. Hyperbaric testing was then repeated. Following the second surfacing, the temperature controller was adjusted back to 21 °C and after 2 h a third set of hyperbaric tests was run. Total test time was 7 h.

b. Test schedule. Five complete tests on each of the 6 field test units were done on separate days: i) 2 tests going from 21 °C to cold and back, ii) 2 tests going from 21 °C to hot

and back, and iii) one control remaining at 21 °C. No temperature tests with the 13 Fleet units were done.

c. Rationale. These tests defined instrument performance at pressure over a temperature range (~10 to 40 °C) that might be experienced during operations.

4. Battery discharge testing

a. Procedures. Analyzers were disconnected from their battery chargers, turned on, and left running overnight. By the next day, the main NICad batteries had discharged enough for the instruments to stop functioning. These batteries were then completely discharged by loading them overnight using a jumper wire containing a 6-volt light bulb. The small backup battery was also discharged using a 150-ohm resistor jumper and waiting for ~2 days. Both batteries were then checked with a voltmeter to confirm little or no voltage (< 1 volts). The analyzers were then attached to the battery chargers and recharged. After about 15 min, instruments could be turned on and operated, although overnight charging was necessary to fully restore the batteries.

b. Test schedule. Because only the 13 Fleet units contained the changes to the battery charging system, these were the only analyzers that were tested.

c. Rationale. Testing confirmed the operation of the charging circuit modification in each analyzer that allowed re-start following complete discharge of both main and backup batteries.

5. Offgas testing

a. Procedures. Analyzers were tested for offgassing by using 10 l Tedlar bags (SKC Inc., Eighty Four, PA) that have very low permeability and are designed for accurate sampling of trace

level contaminants in air. New bags were first filled and emptied 3 times with hydrocarbon-free gas and filled a fourth time and bag valves closed. Bags were then stored in the laboratory (19-24 °C) for at least 24 h to equilibrate prior to baseline sampling. Each bag was then sampled by attaching an evacuated 500-ml stainless steel canister to the bag valve and allowing the canister vacuum to draw gas out via the bag valve and equilibrate at 1 ATA. The canister was subsequently backfilled to 2 ATA with hydrocarbon-free gas to facilitate sample loading into gas chromatographs (GC) to screen for contaminants. After baseline testing, bags were cut open, one analyzer placed into each bag, and bags secured by twisting the Tedlar and attaching a rubber band on the outside. Resampling and analysis of contaminants given off by the analyzer were done after another 24 h.

Gas samples were screened for volatile organic compounds (VOCs) using GC with flame ionization (FID). In some cases, GC with mass spectrometry (MS) was also used to identify species. For GC/FID, gas samples (0.5 ml) were introduced using gas sample valves. For GC/MS (model 5970 Mass Selective Detector; Hewlett-Packard, Rockville, MD), 100 ml of gas was preconcentrated on a solid multibed carbon absorbent (carbotrap 300; Supelco, Inc., Bellefonte, PA). Subsequent thermal desorption at 340 °C for 5 min (Nutech 8533 Universal Sample Concentrator, Nutech Corp., Durham, NC) introduced the sample into the GC. Mass spectrometer scanning was from 20 - 200 amu.

The following column (Supelco, Inc.) was used for analysis of VOCs with the indicated temperature profile for each detector:

VOCOL wide-bore capillary column, 30 m x 0.53 mm, 3.0 μ m film.

FID: 50 °C for 3 min, raised at 8 °C/min to 150 °C for 4.5 min.

GC/MS: -20 °C for 3.1 min, raised at 20 °C/min to 150 °C for 11.4 min.

Organic species were identified, when possible, based on comparison of retention times of sample peaks and of species in commercially acquired, primary gas standards. Identifications were confirmed by comparison of mass spectra. Unknown compounds that did not match retention times of the standards were identified after careful review of library search results. This review was done using Hewlett-Packard G1034C software for the MS ChemStation (DOS series) with the NIST/EPA/MSDC 54K Mass Spectral Database and in view of the limitations inherent in such searches. Where possible, identification was confirmed by direct injection of the suspected chemical species into the GCs.

Quantitation of organic contaminants was based on a primary gravimetric standard of ~10 ppm each of Freon 113, methyl chloroform, benzene, toluene, and xylenes, in hydrocarbon-free air. Individual contaminants, other than these chemicals, were quantified relative to the species in the calibration standard closest to their retention time. Contaminant concentrations were corrected for sample dilution that had occurred when the canisters were backfilled following sampling.

Offgas testing screened for a large number of VOCs including very volatile species (e.g., Freons), less volatile species (e.g., both aliphatics and aromatics), and highly polar species such

as alcohols. Analytical conditions allowed for quantitation of many of these compounds at concentrations ≥ 0.1 ppm, with accuracy estimated at $\pm 20\%$ relative.

b. Test schedule. Three field test units and one Fleet unit were each tested once.

c. Rationale. These tests determined if significant levels of volatile contaminants were being released that might be a hazard during use in the Fleet. Test procedures enhanced the ability to detect contaminants by using low permeability test bags and a small gas volume around the analyzer. For these reasons, contaminant levels measured during this test should be much higher than those that might occur during actual analyzer use where there is a large gas space around the analyzer and ventilation of the DDS is being performed.

6. Testing of displayed pressure reading

No testing of the pressure reading (in fsw) shown on the analyzer display was done.

Field testing

1. Procedures

Field testing of the recommended analyzer was done according to the protocol in Appendix A by SDV personnel and diving medical officers and other personnel from NMRI. The procedures are summarized here. Analyzer calibration was checked and recalibrated (when necessary) on board prior to each operation, using the CAMS-I calibration gas (~15,000 ppm CO₂ in air) or a 15,000 ppm standard supplied by NMRI. Preliminary testing by NMRI demonstrated that the other gaseous components in the CAMS-I gas had no observable effect on

the CO₂ analyzer. During all field testing, analyzer readings were not corrected for the small changes in total pressure that normally occur on submarines.

NAVSEA approval of units for field testing required the analyzers to be hand-held and unmounted during testing (6,7), which limited the time that the units were inside the DDS. Consequently, experience with these analyzers inside the DDS environment was restricted to several hours at a time compared to the 8 or more hours that a DDS operation might last.

The bulk of testing involved recording analyzer measurements during actual DDS operations over a range of conditions (i.e., depths, number of personnel in the compartments, personnel workloads). As opportunities arose, measurements were also taken during the ship's dockside testing. A limited number of gas samples were drawn during each deployment, using NMRI stainless steel canisters, simultaneously when readings were taken with the CO₂ analyzer. These gas samples were analyzed for CO₂ later at NMRI using GC/methanization followed by FID. Prior to analysis, cylinders with low pressure (< 10 psig) were vented to the atmosphere and then backfilled with CO₂-free gas to provide enough pressure to allow loading of GCs. Cylinders of calibration standards were backfilled simultaneously to correct for dilution. Sample cylinders that had sufficient pressure (> 10 psig) were analyzed without backfilling. Carbon dioxide was quantified using a one-point calibration with a primary gas standard close to observed concentrations. These laboratory concentrations were then converted to sev values by multiplying by the pressure inside the DDS compartment recorded at the time of sampling off DDS gauges.

2. Test schedule

The 6 field test units and several Fleet units were tested in pairs (1 spare analyzer per deployment in case of malfunction) on DDS host submarines as deployment schedules permitted.

3. Rationale

Field testing evaluated the draft operating procedures for the analyzer. Calibration data was used to evaluate instrument stability under actual field conditions. Measurements during ventilation were used to estimate effectiveness of current ventilation procedures. Comparison of measurements made in the laboratory with analyzer readings would demonstrate analyzer accuracy under actual DDS operations.

Data analysis

1. Precision

Means and relative standard deviations were calculated from the precision data.

2. Accuracy

Accuracy data were used to calculate relative percent error:

$$\text{Relative percent error} = \frac{\text{Observed reading} - \text{Expected reading}}{\text{Expected reading}} \cdot 100$$

Expected readings were determined as defined earlier.

3. Ambient temperature

Instrument response during cold, hot, and control exposures was calculated (in absolute and percent terms) relative to the initial analyzer readings (first set) taken at 21 °C:

$$\text{Absolute Temperature Response (ppm CO}_2\text{)} = \frac{\text{Reading at test temperature} - \text{Initial reading}}{\text{(cold, hot, or control)} \quad (21 \text{ } ^\circ\text{C})}$$

$$\text{Percent Temperature Response (\%)} = \frac{\text{Absolute Temperature Response} \bullet 100}{\text{Initial reading (21 } ^\circ\text{C)}}$$

Analyzer recovery from the temperature exposure after return to 21 °C was also calculated relative to the initial readings:

$$\text{Absolute Temperature Recovery (ppm CO}_2\text{)} = \text{Last Reading (21 } ^\circ\text{C)} - \text{Initial reading (21 } ^\circ\text{C)}$$

$$\text{Percent Temperature Recovery (\%)} = \frac{\text{Absolute Temperature Recovery} \bullet 100}{\text{Initial reading (21 } ^\circ\text{C)}}$$

4. Error in calibration gas standards

Results will reflect the error of $\pm 1\%$ relative associated with the reported CO₂ concentrations of the gas standards.

5. Field testing

Field test data were used to calculate the relative percent error of the analyzer compared to the CO₂ concentration based on laboratory analysis of the canister gas samples:

$$\text{Relative percent error} = \frac{\text{Analyzer value} - \text{Lab value}}{\text{Lab value}} \bullet 100$$

In this case, the expected or "true" value is assumed to be the lab value. As will be discussed later, significant error is probably associated with the lab value.

RESULTS AND DISCUSSION

Laboratory testing

1. Precision

Relative standard deviations based on 5 measurements of 1.5% CO₂ over 10 min were < 1% for all instruments (Tables 3 and 4). No problem with zero drift was observed with any instruments; when presented with CO₂-free gas, analyzers in all cases read within 100 ppm of zero.

Conclusion. All 6 analyzers tested met the desired $\pm 5\%$ short-term repeatability requirement.

2. Ambient pressure accuracy

After calibration with 15,000 ppm (1.5%) CO₂, the measurement error for all instruments was $\leq 10\%$ for concentrations from 25,000 ppm (2.5%) down to at least ~1,500 ppm (Figs. 3 and 4). At the lower CO₂ concentrations, relative errors increased. This reflects the tendency for small absolute errors at these levels to translate into large relative errors. However, results clearly show that there are significant differences among analyzers in accuracy and response with some units able to read CO₂ levels considerably below 1,500 ppm to within 10%. Little difference was observed between results done on 2 consecutive days without recalibration of the analyzer.

Instruments read humidified gas several percentage points lower than dry gas. It should be noted that humidified gas tests were done only with the 6 field test units (Fig. 3). However, measurement error with humidified gas was still within 10% of expected value. Analyzer

calibration using 1,000 ppm improved measurement accuracy around this level of CO₂ to $\leq 10\%$ for all analyzers (Fig. 5). No problem with zero drift was observed with any instruments; when presented with CO₂-free gas, analyzers in all cases read within 100 ppm of zero.

Conclusion. All 19 analyzers met the desired $\pm 10\%$ short-term accuracy requirement at ambient pressure down to concentrations $\sim 1,500$ ppm for both dry and humidified gas.

Recalibration using 1,000 ppm CO₂ improved accuracy at lower levels of CO₂.

3. Hyperbaric accuracy

Except for some of the measurements at lower concentrations, analyzers generally had relative errors to within 10% for CO₂ concentrations from 1,500 to 25,000 ppm (2.5%) sev at pressures from 1 to 6 ATA (see upper graphs for each analyzer in Figs. 6-8). This was true for both dry (Figs. 6 and 7) and humidified gas (Fig. 8). As was the case with ambient pressure testing, little difference ($< 5\%$) was usually observed between results obtained on 2 consecutive days without recalibration of the analyzer (see lower graphs in Figs. 6-8). The effect of humidified gas was generally much less than 10% when comparing wet-to-dry measurements made on the same day (Fig. 9). Again, significant differences in responses were observed among some of the instruments.

After analyzers were reset to factory calibration, relative measurement errors generally remained within 10% (see upper graphs for each analyzer in Fig. 10), although readings were often substantially different from those obtained with lab calibration (see lower graphs in Fig.

10). No problem with zero drift was observed with any instruments; when presented with CO₂-free gas, analyzers in all cases read within 100 ppm of zero.

Conclusion. All 19 analyzers met the desired $\pm 10\%$ short-term accuracy requirement for CO₂ measurements from 1,500-25,000 ppm (2.5%) sev at pressures from 1-6 ATA for both dry and humidified gas. Resetting to factory calibration is a reliable option in the field when normal calibration cannot be done.

4. Effect of ambient temperature

Instrument readout during hyperbaric testing changed less than 300 ppm, or $\pm 5\%$ of reading, after 2 h cooling or heating compared to the first set of results obtained at 21 °C prior to temperature change (see first page of Fig. 11). Average cold and hot test temperatures were 13 °C and 41 °C. These changes are similar to the control responses observed when analyzers were left at 21 °C for 2 h and then retested (see second page of Fig. 11). In both cases, the changes in readout appeared to be randomly distributed about zero. When analyzers were returned to 21 °C (or left at 21 °C for the control tests) and tested a third time, similar changes, relative to the first set of data were observed (Fig. 12).

Conclusion. Temperature (ranging from 13 °C to 41 °C) appeared to have little, if any, effect on the analyzers.

5. Battery discharge testing

All 13 analyzers that were tested restarted without any problem following ~15 min recharging after complete discharge of both main and backup batteries. Overnight recharging restored all batteries to full capacity.

Conclusion. The charging circuit modification worked correctly in all 13 analyzers.

6. Offgas testing

Only very low levels of a number of volatile organic compounds were detected during the offgas testing of 3 field test and 1 Fleet analyzers. The principal species that were identified were ~1-2 ppm methyl ethyl ketone, < 1 ppm toluene, and < 1 ppm xylenes. A number of other volatile organic compounds (VOCs) were also detected at individual levels estimated at < 2 ppm. Total VOCs were estimated to range from 4-8 ppm. Results appeared to be similar among the 4 analyzers tested.

Conclusion. The low level of offgassing observed from analyzers tested should cause no safety concern.

Field testing

Field test data were collected from August 1995 to August 1997 during 13 separate deployments on 5 of the 7 DDS host submarines and during a week-long training exercise at the DDS training facility at Little Creek, VA (Table 5). This testing produced a total of 85 reportable data pairs of simultaneous analyzer readings and CO₂ concentrations based on subsequent laboratory analysis of canister gas samples. These data consisted of 35 samples from the hangar,

31 from the trunk, and 19 from the treatment chamber (Figs. 13-15) taken at pressures from surface (1 ATA) up to 4.9 ATA (130 fsw). Analyzer and laboratory values generally agreed closely (see top graphs in Figs. 13-15) with relative errors typically < 25% for the hangar and treatment chamber and somewhat greater for the trunk (see bottom graphs).

The level of agreement between analyzer and laboratory values is quite remarkable considering the large number of potential errors associated with the test. The analyzer error in CO₂ measurement would be analogous to the accuracy determined in the laboratory, but was determined under actual field conditions with submarine internal pressure ignored. However, in the field, the sample gas inside the DDS is not only fluctuating in CO₂, but is unknown in concentration. The canister sampling procedures on the submarine and analytical procedures conducted later back in the laboratory, which were required to estimate the actual pressure-corrected concentration during the test, would be expected to add significant error (perhaps up to 20% relative) to the final test result. For example, it probably was difficult at times to obtain canister samples that were representative of the gas sampled by the analyzer inside a compartment crowded with working divers who are producing substantial CO₂. This may explain the greater error associated with the measurements in the trunk, which was small and often contained a large number of divers.

In addition to the 85 data pairs reported here, a number of other data were omitted from this report. Other pairs of analyzer/canister measurements were excluded if any of the following applied: 1) canister valve(s) leaked during transit, as indicated by lack of canister pressure for

pressurized samples or CO₂ levels in a canister < 400 ppm indicative of normal air, 2) canister valve(s) found open upon delivery at NMRI; 3) data recorded incorrectly or incompletely, preventing its use; 4) samples labeled as suspect by the field test personnel due to known procedural errors during sampling; or 5) analyzer reading and lab-derived value different by a factor of 2 or more. The first 4 exclusion criteria eliminated data that could be objectively judged to be invalid. The last criterion eliminated 8 outlying data pairs that, for the purposes of this report, were considered to be in such disagreement to be explainable only by human mistakes made in the field and/or the lab.

In addition to the data pairs, a large number of analyzer readings were recorded during DDS operations (without canister samples) to estimate effectiveness of current ventilation procedures during operations. These data will not be discussed in detail, because the data in Figs. 13-15 are representative showing a wide range in CO₂ concentrations during DDS operations that were often substantially lower or higher than the current limit of 15,000 ppm (1.5%). However, there were some instances where analyzer measurements exceeded 25,000 ppm during testing in the trunk with as many as 7 divers and in the hangar with up to 10 divers.

Conclusion. Field testing during DDS operations demonstrated the analyzer generally agreed closely with subsequent laboratory analysis of canister air samples, despite inherent errors of the overall test. Results indicated that current ventilation procedures often overventilated or underventilated the compartments of the DDS.

General performance

1. Laboratory

Nineteen hyperbaric analyzers were tested for hundreds of hours in the laboratory and, with relatively few exceptions, performed flawlessly. The major problem encountered during laboratory testing was an unexpected lockup by several of the Fleet analyzers when initially compressed. This problem was traced by the manufacturer to an electrical contact occurring on the main circuit board when the case flexed during compression; this has now been corrected.

2. Field

Analyzers were generally well received by Fleet personnel during the extensive field testing that occurred over a 2-year period. Results indicated that analyzers worked reliably in the field, but were not indestructible particularly in light of the harsh environment to which they were subjected. Most of the problems arose toward the end of this study with the 6 field test units. These units had been initially acquired more than 2 years earlier and had been exposed to considerable transport and use in the field. All 6 instruments had been taken apart and extensively modified several times by the manufacturer in their factory during the development phase, which may have increased the likelihood for later problems.

Several analyzers, returned to NMRI from the field, did not operate correctly or at all. Inspection of the shipping case and subsequent repair suggested severe shock or abuse had occurred during transport. Identified problems included an intermittent sampling pump malfunction in one unit and a loose detector in another. Water entered the battery compartments

in 2 units causing battery damage in 1 of them; the waterproofing design was subsequently changed to address this problem. All 6 original field test units were returned to the manufacturer in August 1997 for a complete evaluation to learn more about their tolerance to field use. No particular parts of any of these analyzers showed sign of excessive wear. However, some of the analyzers had a white powdery deposit on the inside of the aluminum infrared source block. This had never been seen before by the manufacturer and was assumed to be related in some manner to salt water exposure.

SUMMARY

1. The hyperbaric CO₂ analyzer developed by NMRI meets the requirements for use in the DDS as defined earlier. The laboratory and field test results indicate that the analyzer should satisfy the 20% accuracy requirement that has been deemed adequate by a U.S. Navy Working Group for monitoring CO₂ in the DDS (2).

2. Considerable testing both in the laboratory and field indicates that the analyzers should work reliably in the Fleet. The fact that analyzers were field tested inside the DDS for less time than an actual DDS operation may last is not considered important in terms evaluating analyzer reliability. However, as with any new piece of gear, instrument performance should be carefully monitored during the transition to the Fleet to detect unforeseen problems.

3. The significant differences among analyzers that were seen during testing suggest that all analyzers be tested in the laboratory for reliability prior to delivery to the Fleet.

4. Recommended operating procedures are given in Appendix B.

5. In addition to meeting the requirements for CO₂ measurement during DDS operations, this analyzer may also fill the existing need for reliable CO₂ measurement inside other types of hyperbaric chambers and diving apparatus.

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7. NAVSEA letter 9510/DDS, serial #395A22/175 of 22 Nov 1995.

Table 1. Analyzers tested.

Serial numbers given in table.

Field test units	Fleet units	
DS001	125	133
DS002	126	134
DS007	127	135
HB062	128	136
HB063	131	138
HB076	132	142

Table 2. Gas standards and test pressures used during hyperbaric testing.

Values in the table are sev concentrations delivered to the analyzer in ppm.

Chamber pressure (ATA)	Gas standard concentration (ppm)					
	1,500	2,500	3,000	3,750	5,000	15,000
1	1,500	2,500	3,000	3,750	5,000	15,000
2	3,000	5,000	6,000	7,500	10,000	15,000
3	4,500	7,500	9,000	11,250	15,000	22,500
4	6,000	10,000	12,000	15,000	20,000	
5	7,500	12,500	15,000	18,750	25,000	
6	9,000	15,000	18,000	22,500		

Bold values are current DDS CO2 limits.

Table 3. Ambient pressure precision - Field test units.

		Week1	Week2	Week3	Week4
#DS001	Mean (ppm)	-	14840	14380	14540
	R.S.D. (%)	-	0.15	0.29	0.26
	Range	-	14820-14880	14340-14440	14480-14580
#DS002	Mean (ppm)	-	14840	14380	14500
	R.S.D. (%)	-	0.32	0.21	0.20
	Range	-	14780-14880	14340-14420	14460-14540
#HB062	Mean (ppm)	15040	14960	14800	14880
	R.S.D. (%)	0.22	0.20	0.18	0.41
	Range	15020-15100	14940-15020	14780-14840	14800-14960
#HB063	Mean (ppm)	14940	14680	14780	14780
	R.S.D. (%)	0.22	0.30	0.27	0.30
	Range	14920-15000	14640-14740	14740-14840	14760-14860
#DS007	Mean (ppm)	14620	14760	15020	14700
	R.S.D. (%)	0.31	0.27	0.17	0.24
	Range	14580-14680	14720-14800	15000-15060	14660-14760
#HB076	Mean (ppm)	15000	14880	14540	14980
	R.S.D. (%)	0.22	0.24	0.18	0.24
	Range	14960-15040	14840-14920	14520-14580	14940-15020

R.S.D. = relative standard deviation (n = 5 in all cases)

Table 4. Ambient pressure precision - Fleet units.

		Week1	Week2			Week1	Week2
#125	Mean (ppm)	14660	14680	#133	Mean (ppm)	14540	14500
	R.S.D. (%)	0.07	0.12		R.S.D. (%)	0.26	0.27
	Range	14660-14680	14640-14680		Range	14480-14580	14480-14560
#126	Mean (ppm)	14520	14800	#134	Mean (ppm)	14480	14700
	R.S.D. (%)	0.16	0.18		R.S.D. (%)	0.21	0.30
	Range	14500-14560	14760-14820		Range	14440-14520	14640-14760
#127	Mean (ppm)	14780	14840	#135	Mean (ppm)	14500	14660
	R.S.D. (%)	0.24	0.25		R.S.D. (%)	0.21	0.12
	Range	14740-14840	14780-14880		Range	14460-14540	14640-14680
#128	Mean (ppm)	14820	14540	#136	Mean (ppm)	14840	14980
	R.S.D. (%)	0.10	0.12		R.S.D. (%)	0.18	0.12
	Range	14800-14840	14520-14560		Range	14800-14860	14960-15000
#131	Mean (ppm)	14820	14940	#138	Mean (ppm)	14780	14480
	R.S.D. (%)	0.20	0.26		R.S.D. (%)	0.48	0.21
	Range	14780-14860	14900-15000		Range	14660-14840	14440-14520
#132	Mean (ppm)	14740	14440	#142	Mean (ppm)	14440	14700
	R.S.D. (%)	0.26	0.08		R.S.D. (%)	0.12	0.31
	Range	14680-14780	14420-14440		Range	14440-14480	14660-14760

R.S.D. = relative standard deviation (n = 5 in all cases)

Table 5. Field tests completed.

Submarine	Testing Dates
USS ARCHERFISH (SSN 678)	08/95 5/96 - 6/96 07/96 08/96
USS WILLIAM H. BATES (SSN 680)	07/97
USS KAMEHAMEHA (SSN 642)	11/96 04/97- 05/97 06/97
USS JAMES K. POLK (SSN 645)	12/95 05/96 06/96 09/96 - 11/96
USS L. Mendel Rivers (SSN 686)	04/97
Little Creek training facility	08/97

FIGURE LEGENDS

Figure 1.

Hyperbaric test system. Delivers test gases to multiple analyzers under pressure.

Figure 2.

Ambient pressure test system. Delivers test gases to multiple analyzers at ambient pressure via the STEC gas divider.

Figures 3-4.

Ambient pressure accuracy - Field test units (Fig. 3) or Fleet units (Fig. 4). Measurement error vs. CO₂ concentration for 2 consecutive test days for each of 4 weeks (Field test units) or 2 weeks (Fleet units). Analyzers calibrated with 15,000 ppm CO₂ at beginning of each week's testing. STEC gas divider then used to deliver 0 to 100 to 0% of the gas standard concentration using both dry and humidified (wet) gas. Two gas standards used: 2.5% and 0.25%. Gas standard and analyzer serial numbers given at top of each graph.

Figure 5.

Ambient pressure accuracy - 1000 ppm calibration - Fleet units. Graphs compare measurement error after calibration with 15,000 ppm CO₂ (high cal) to error after calibration with 1,000 ppm (low cal). Testing done for each of 2 weeks. STEC gas divider used to deliver 0 to 100 to 0% of the 0.25% gas standard using dry gas. Analyzer serial numbers given at top of each graph.

Figs. 6-7.

Hyperbaric accuracy using dry gas - Field test units (Fig. 6) or Fleet units (Fig. 7). Measurement error vs. test pressure for 2 consecutive test days for each of 4 weeks (Field test units) or 2 (Fleet units) weeks. Top graph gives the first day results and the bottom graph the difference between day 1 and day 2 of each week. Analyzers calibrated with 15,000 ppm CO₂ at beginning of each week's testing. Seven gas standards (in legend) delivered to analyzers as pressures varied from 1 ATA to 6 ATA and the back to 1 ATA. Analyzer serial numbers given at top of each graph.

Figure 8.

Hyperbaric accuracy using wet gas - Field test units. Measurement error vs. test pressure for 2 consecutive test days for each of 4 weeks. Top graph gives the first day results and the bottom graph the difference between day 1 and day 2 of each week. Analyzers calibrated with 15,000 ppm CO₂ at beginning of each week's testing. Four gas standards (in legend) delivered, after being humidified, to analyzers as pressures varied from 1 ATA to 6 ATA. Analyzer serial numbers given at top of each graph.

Figure 9.

Effect of water vapor on hyperbaric accuracy - Field test units. Difference in measurement error between dry (Fig. 6) and wet (Fig. 8) testing for 2 consecutive test days for each of 4 weeks. Analyzer serial numbers given at top of each graph.

Figure 10.

Hyperbaric accuracy - factory calibration - Fleet units. Measurement error after reset to factory calibration for each of 2 weeks. Top graph gives the factory calibration results and the bottom graph the difference between laboratory calibration and factory calibration. Analyzer serial numbers given at top of each graph.

Figure 11.

Response to temperature change - Field test units. Change in analyzer reading during 2 cold, 2 hot, and 1 control exposures vs. test pressure for 6 analyzers (in legend) and 4 gas standards (at top of graph). Analyzer response given in both absolute (top graphs) and percent (bottom graphs) terms.

Figure 12.

Recovery from temperature exposure - Field test units. Difference between analyzer reading at 21 °C before and after temperature exposure. Difference given both in absolute (top graphs) and percent (bottom graphs) terms for the 6 analyzers (in legend).

Figures 13-15.

Hangar (Fig. 13), Trunk (Fig. 14), and Chamber (Fig. 15) field test data. CO₂ values measured with the analyzer in the 3 DDS compartments compare well with values based on subsequent laboratory analysis of canister gas samples (see top graphs). The line drawn represents perfect agreement between lab and analyzer values. The bottom graphs show the relative analyzer error for each lab value.

Figure 1. Hyperbaric test system.

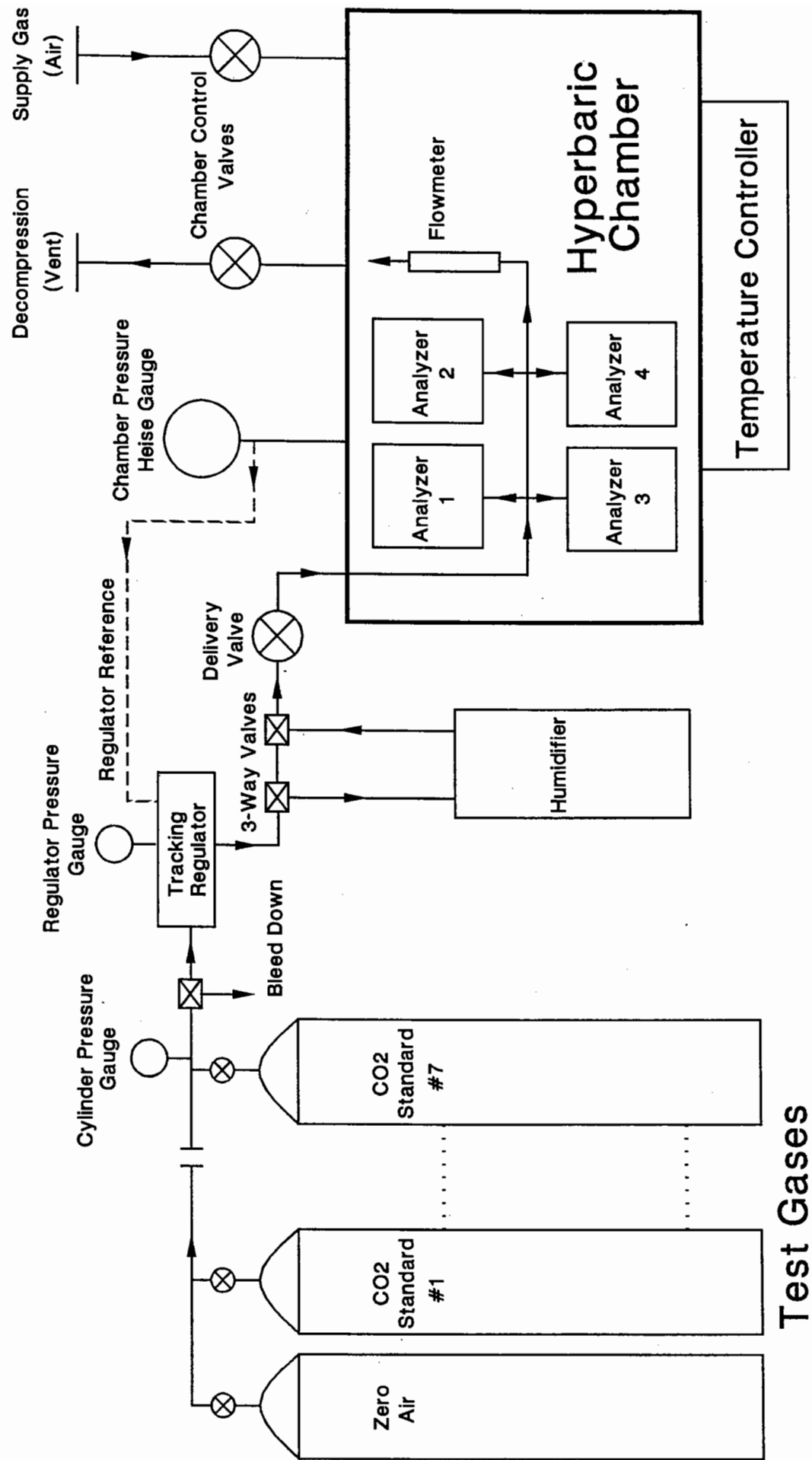


Figure 2. Ambient pressure test system.

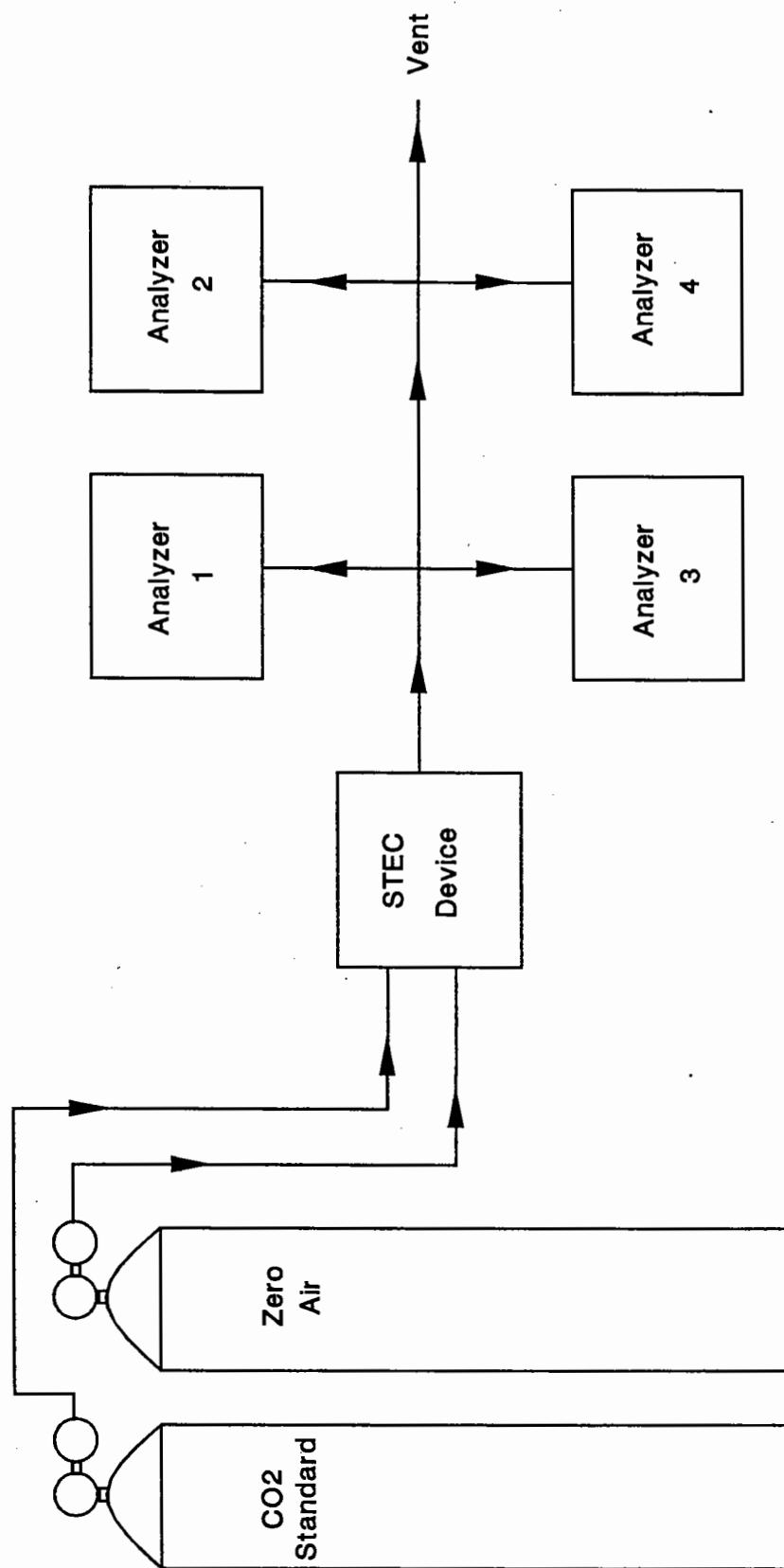


Figure 3. Ambient pressure accuracy - Field test units.

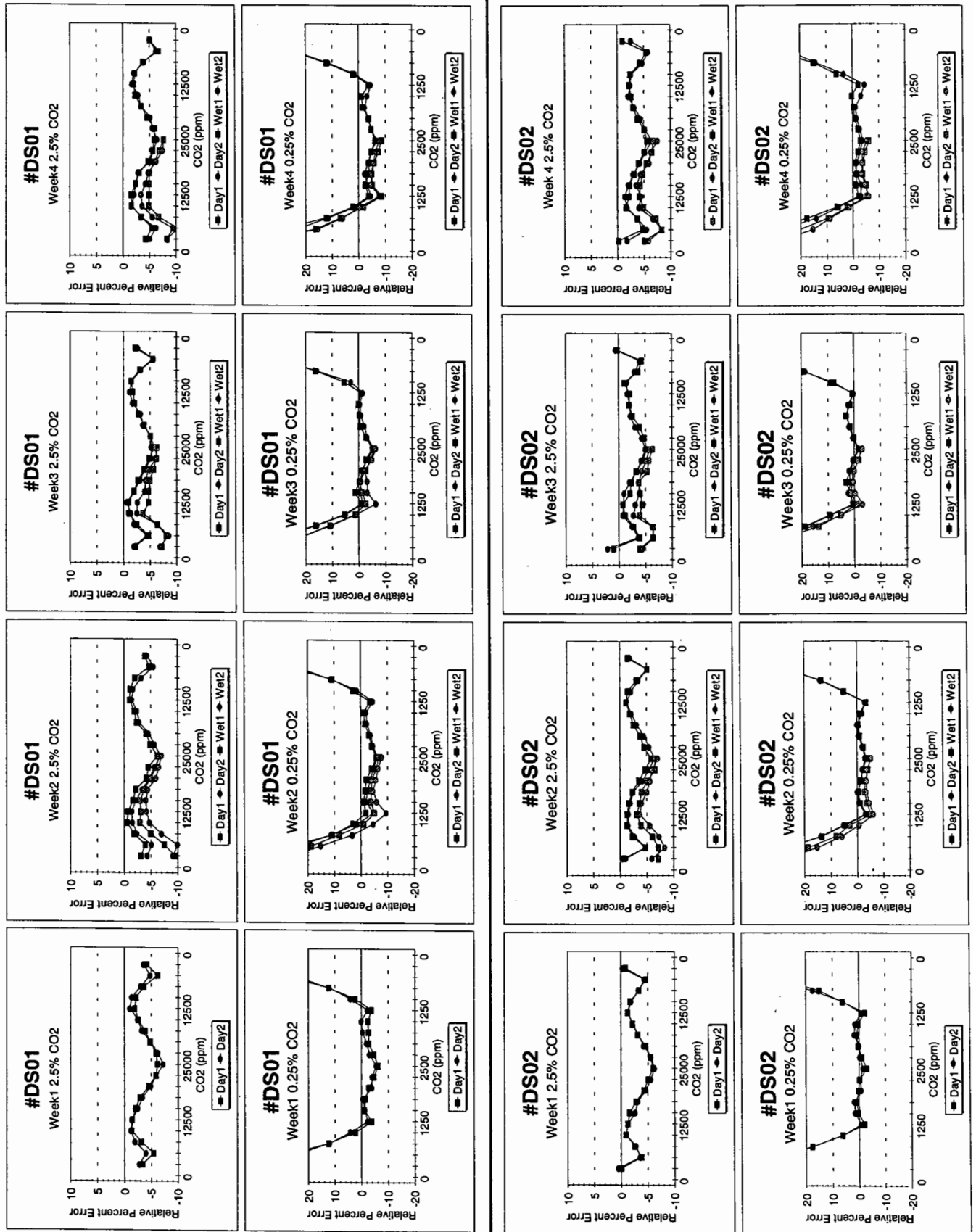


Figure 3. (cont.)

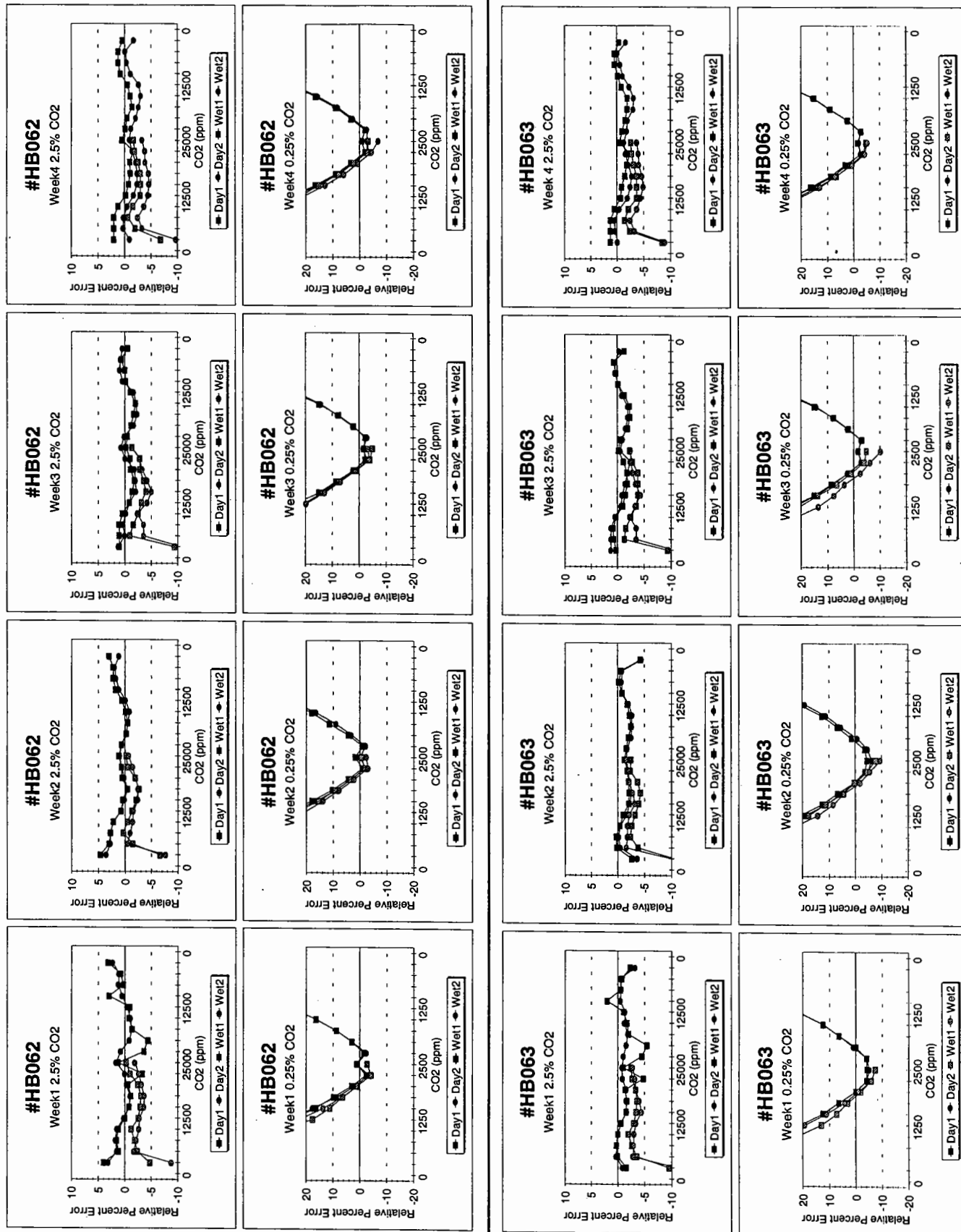


Figure 3. (cont.)

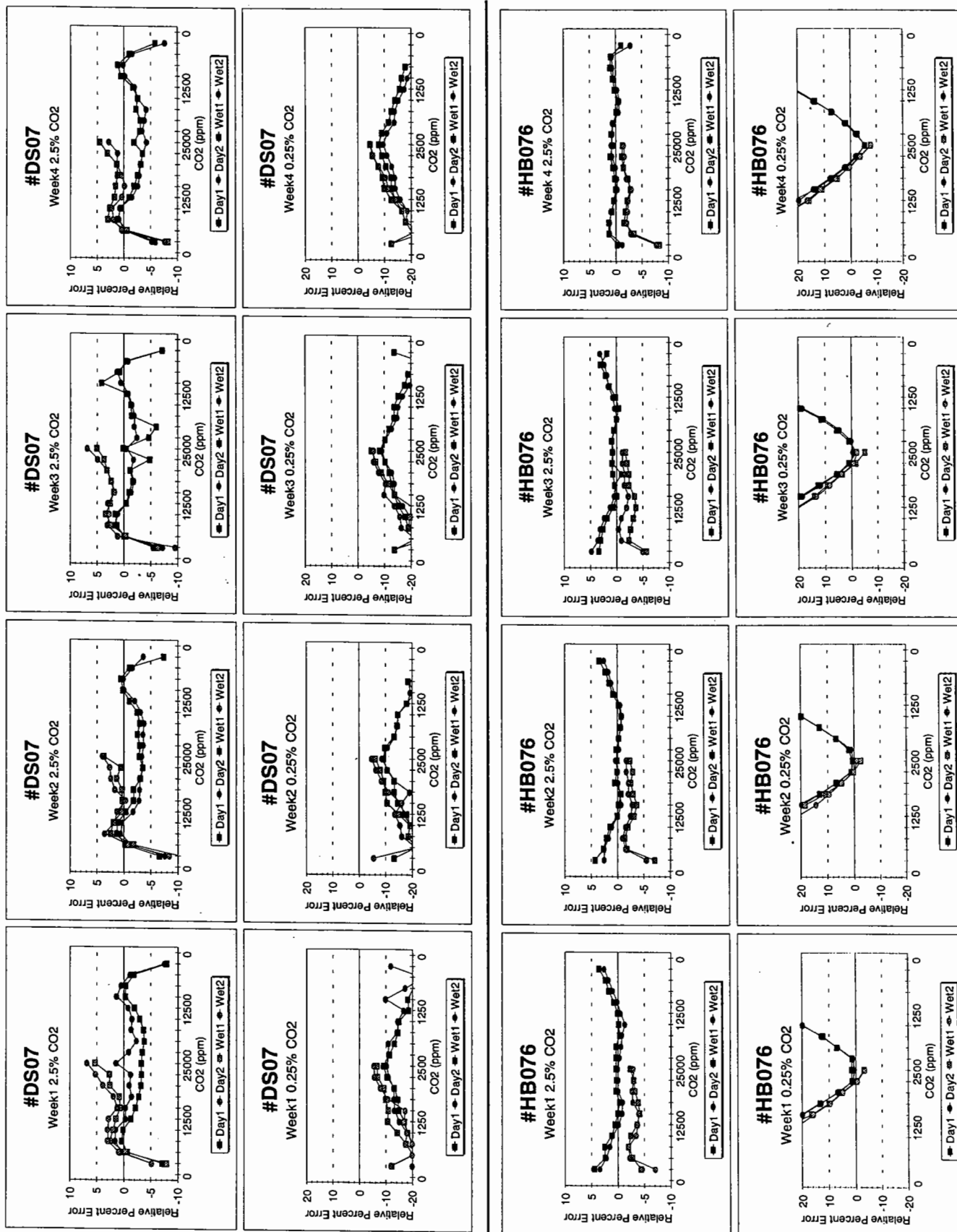


Figure 4. Ambient pressure accuracy - Fleet units.

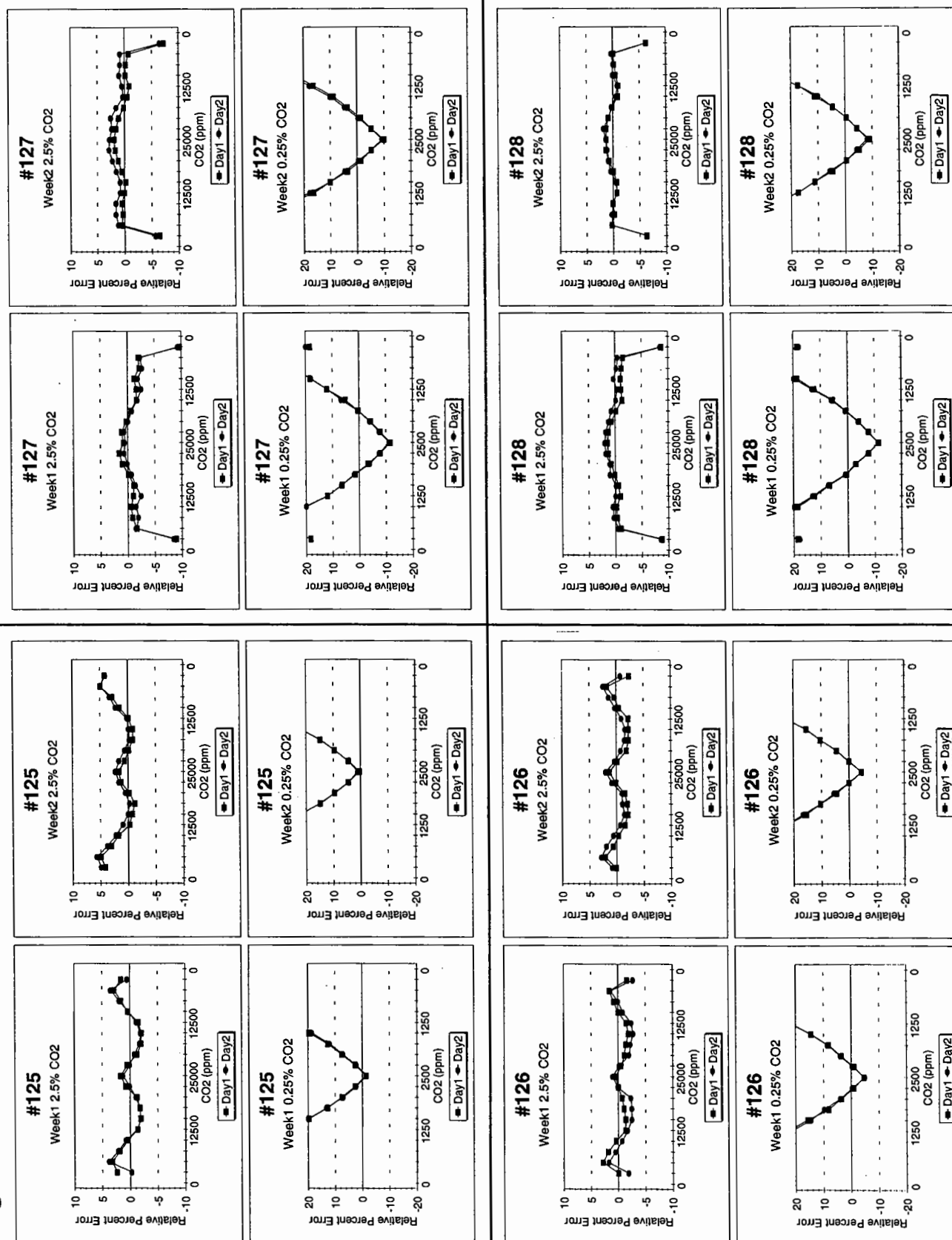


Figure 4. (cont.)

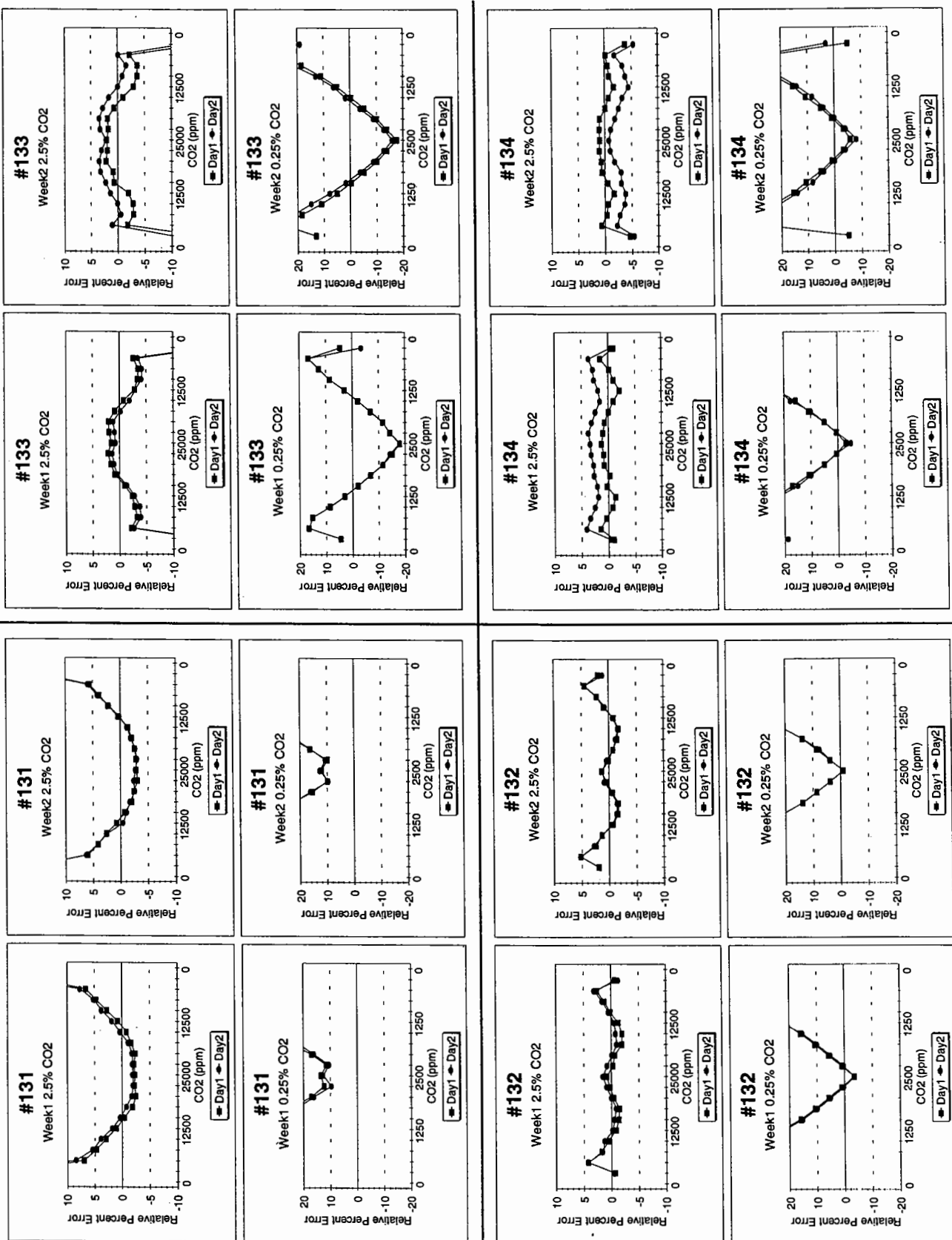


Figure 4. (cont.)

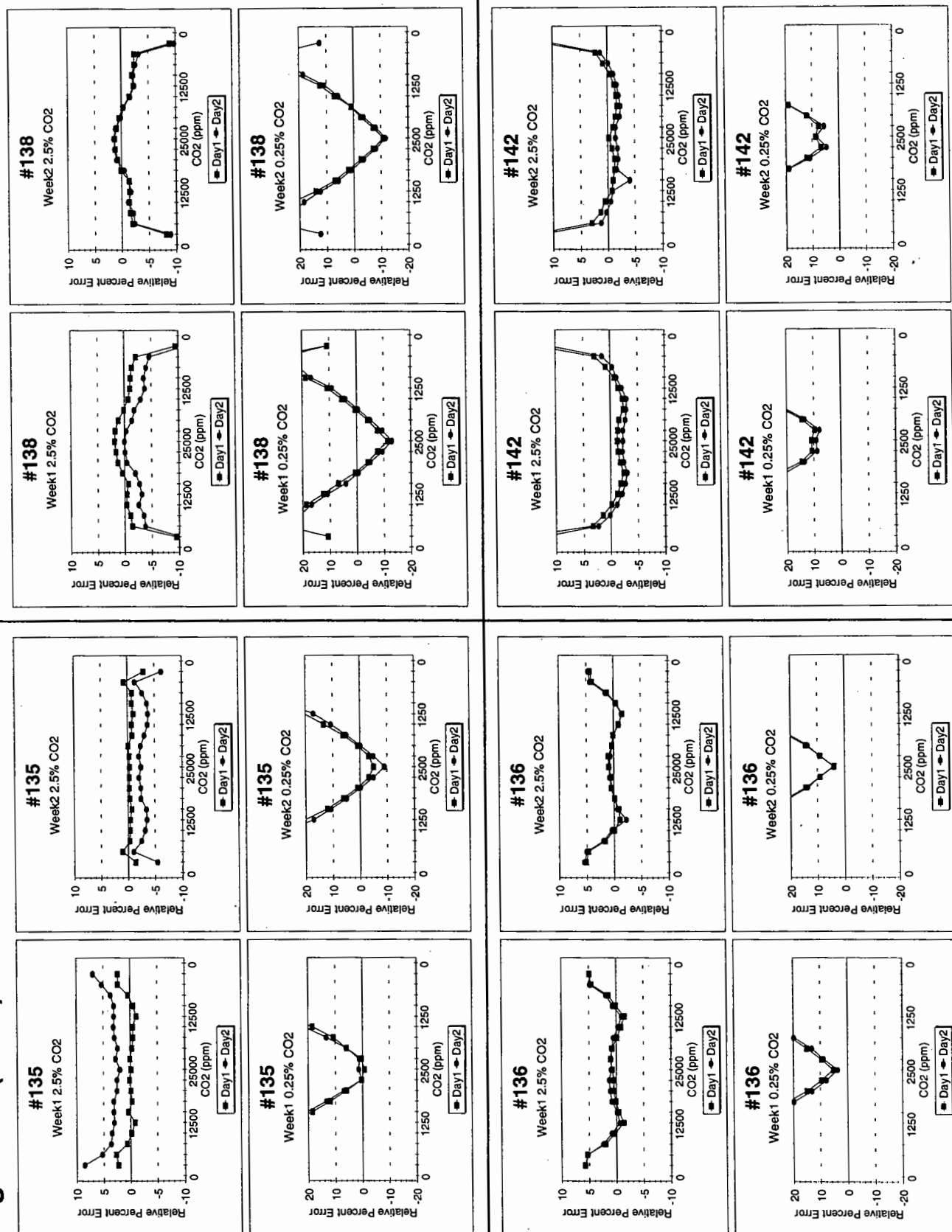


Figure 5. Ambient pressure accuracy - 1000ppm calibration - Fleet units.

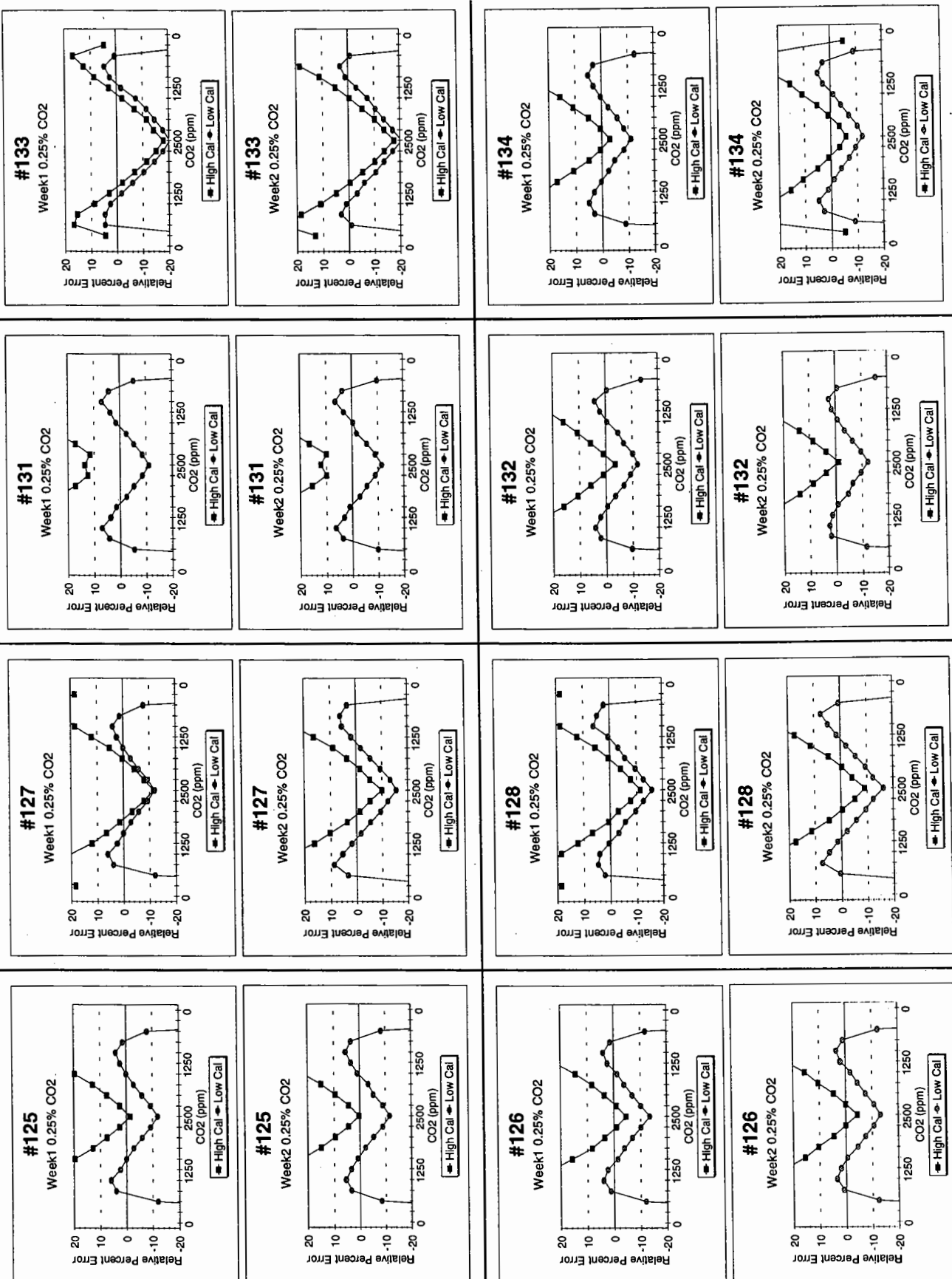


Figure 5. (cont.)

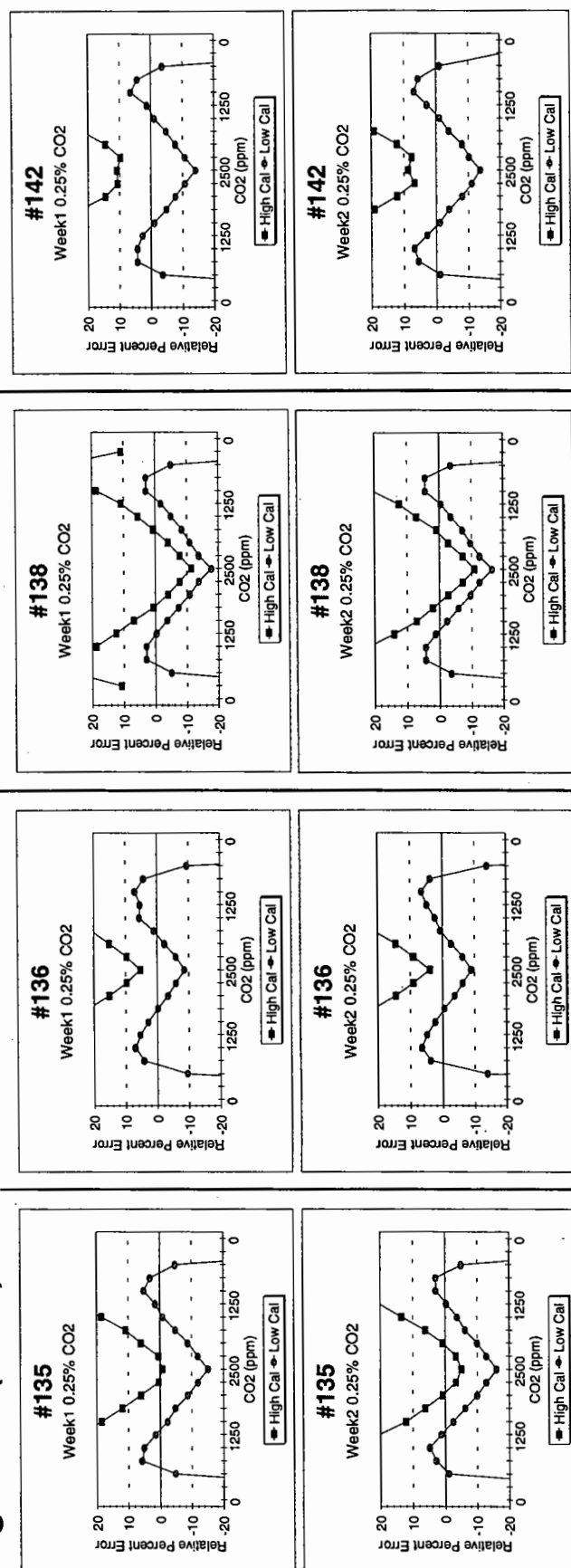


Figure 6. Hyperbaric accuracy using dry gas - Field test units.

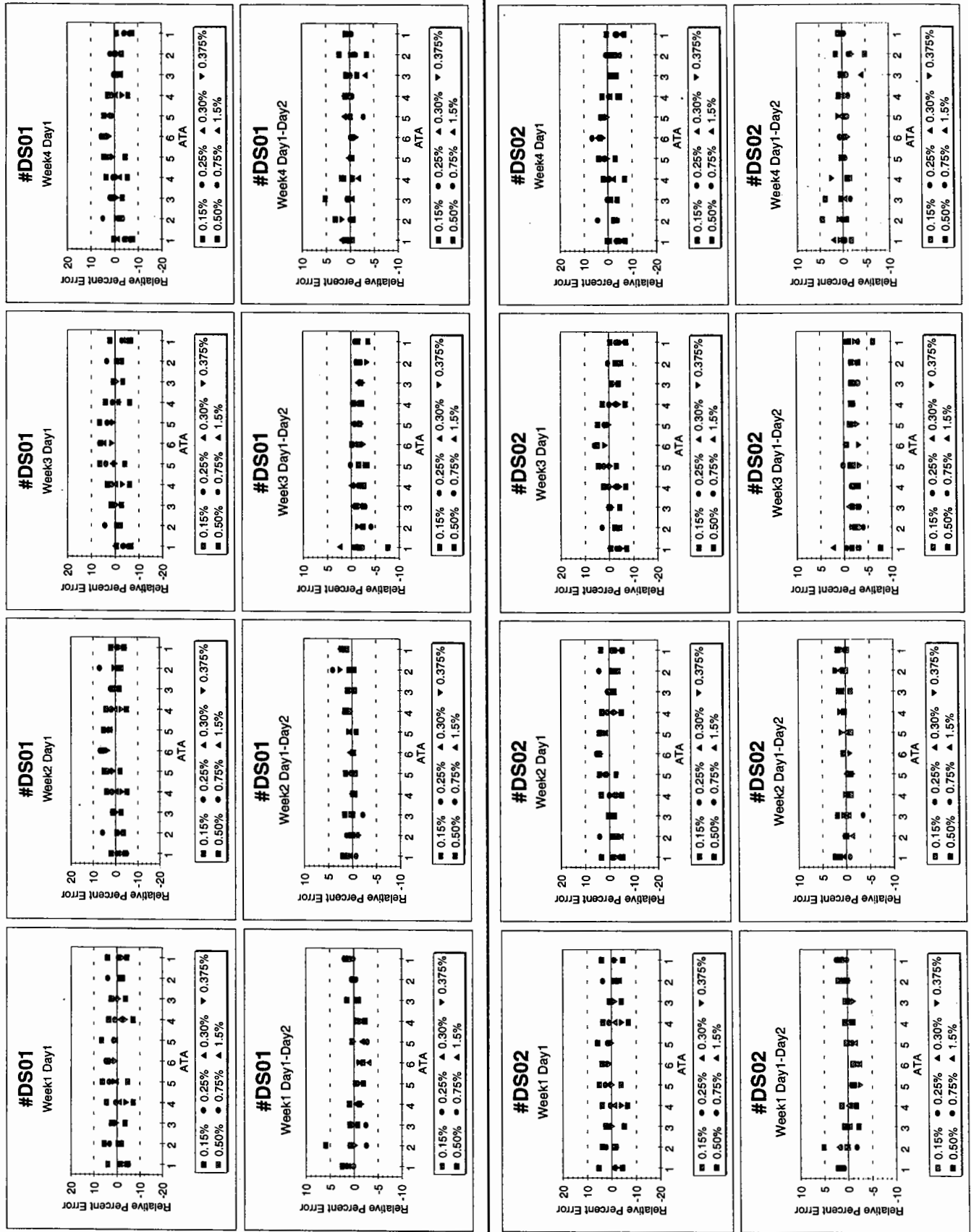


Figure 6. (cont.)

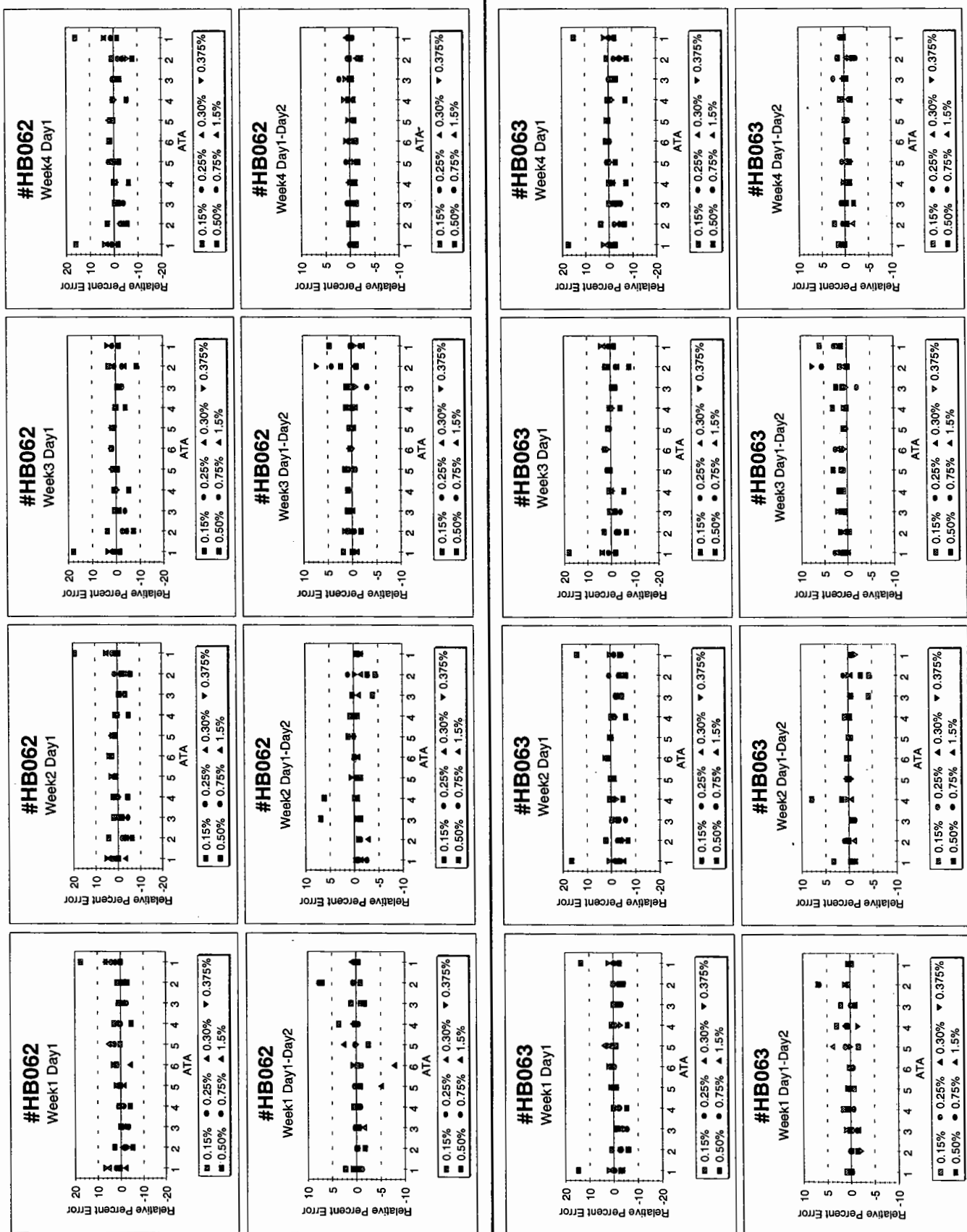


Figure 6. (cont.)

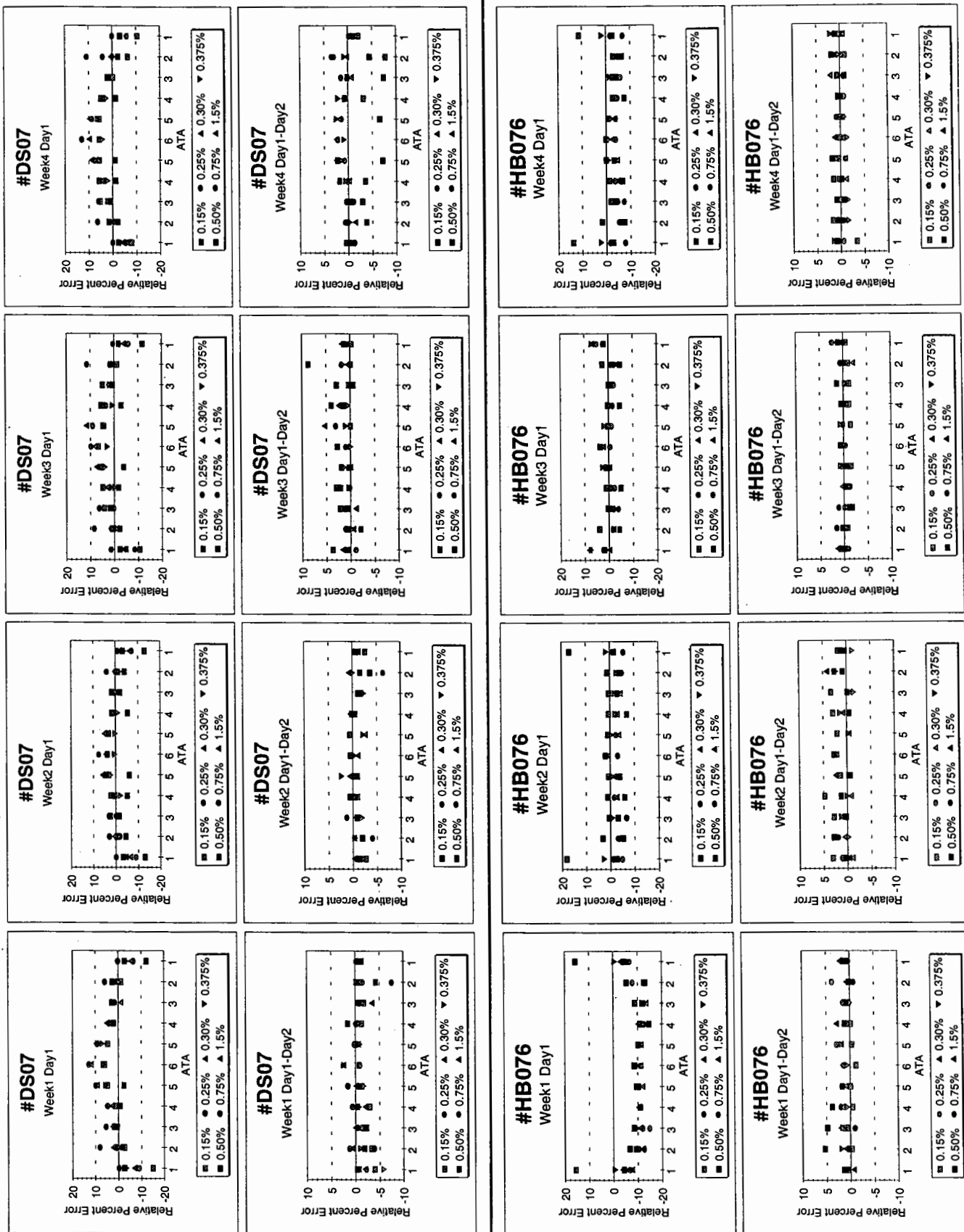


Figure 7. Hyperbaric accuracy using dry gas - Fleet units.

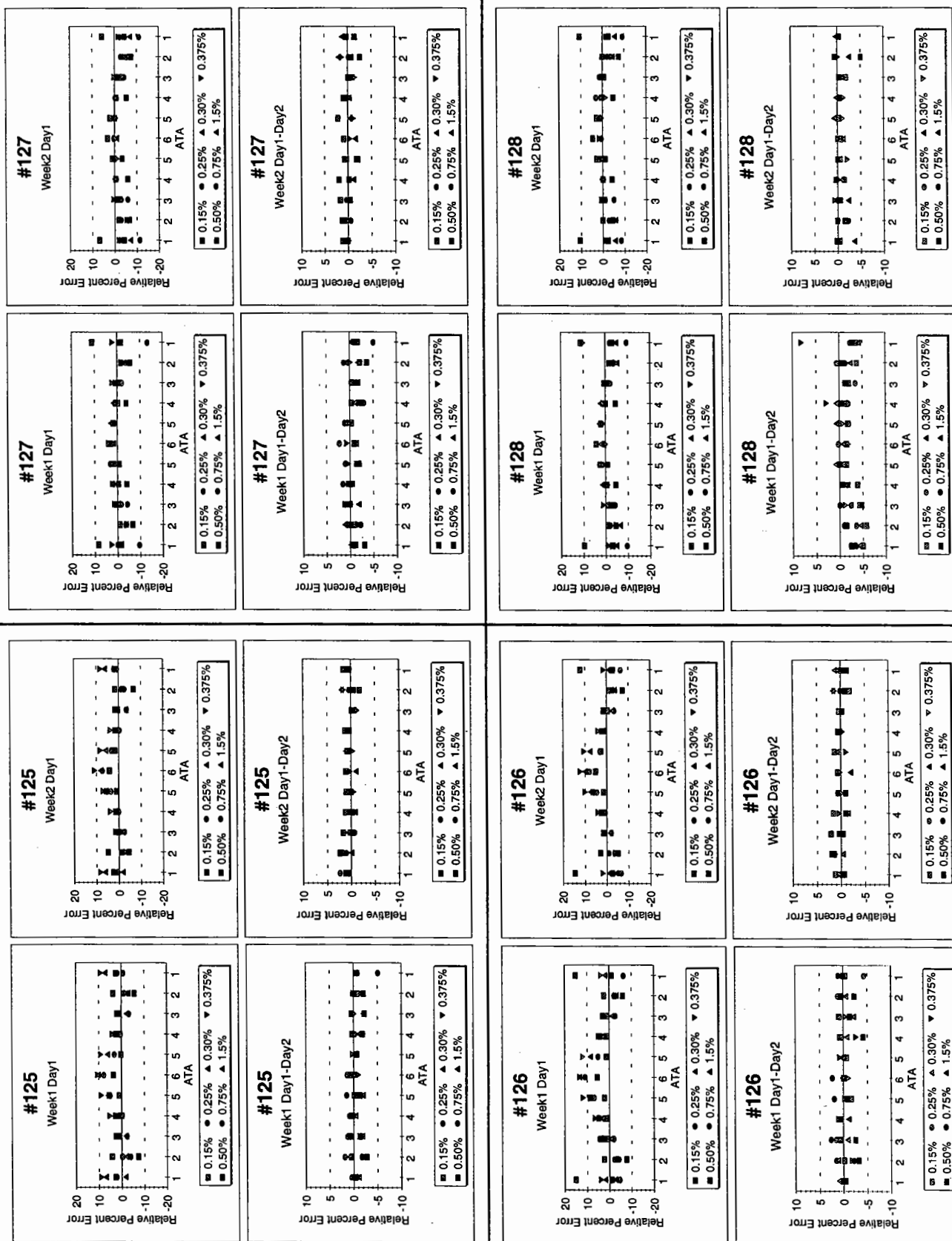


Figure 7. (cont.)

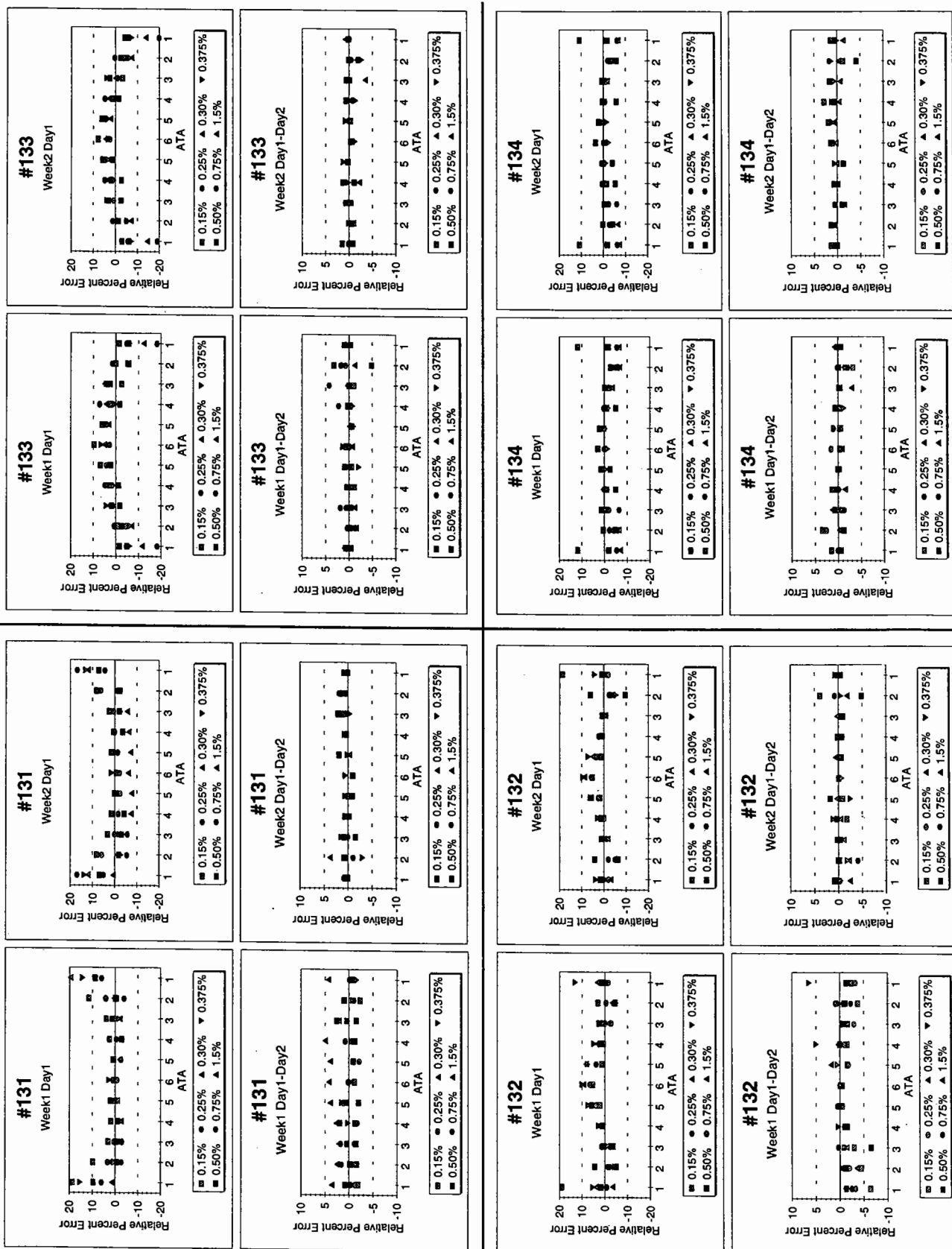


Figure 7. (cont.)

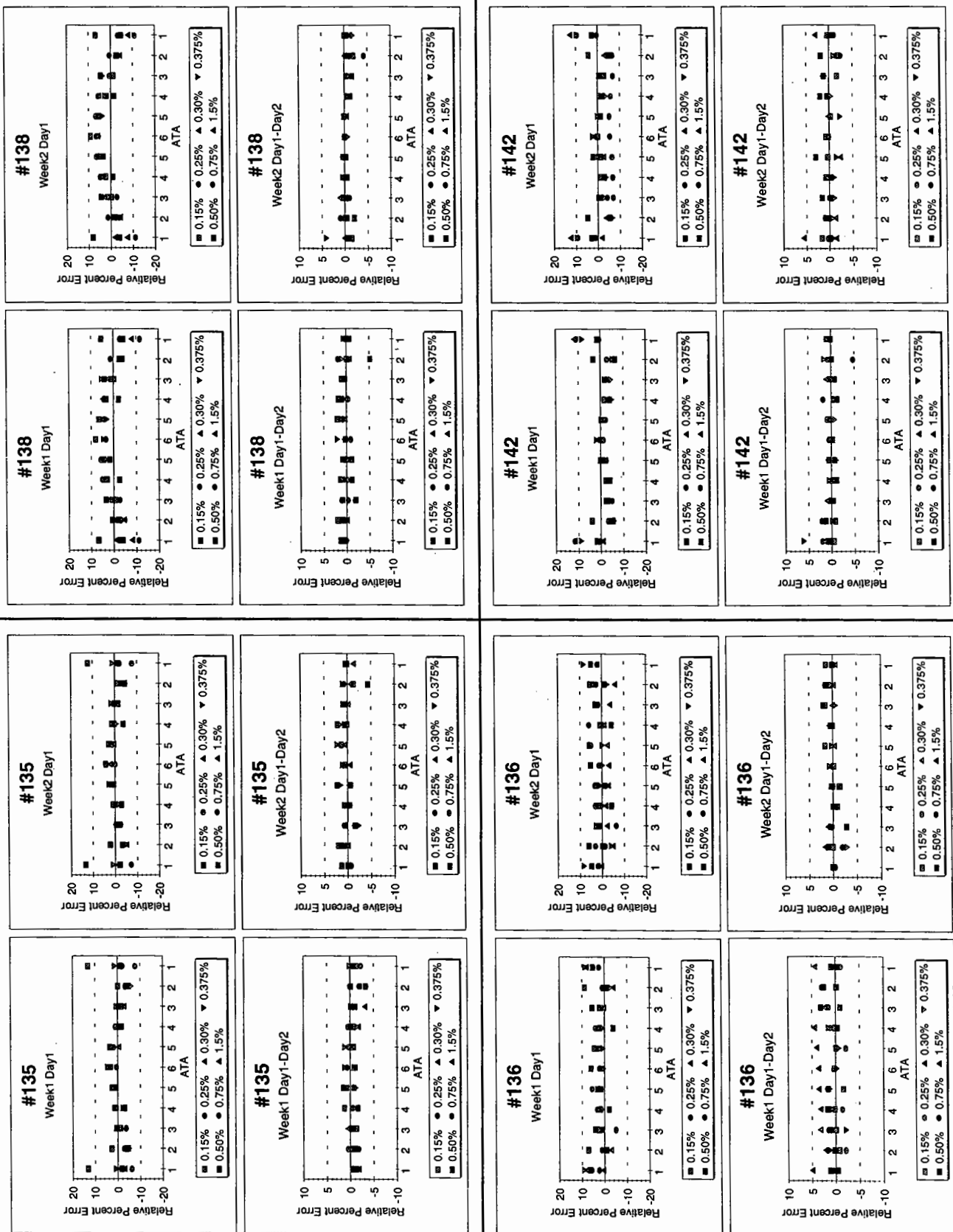


Figure 8. Hyperbaric accuracy using wet gas - Field test units.

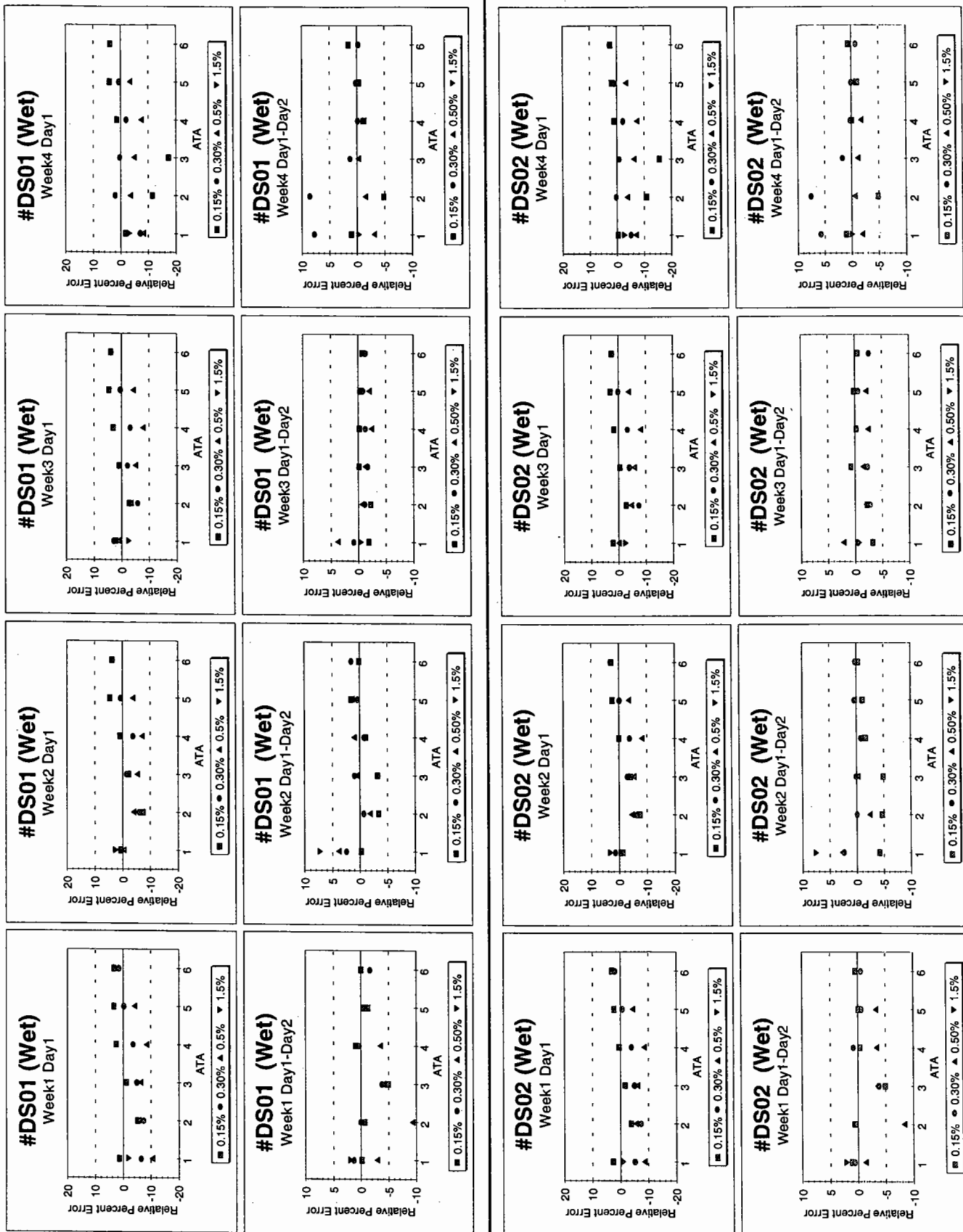


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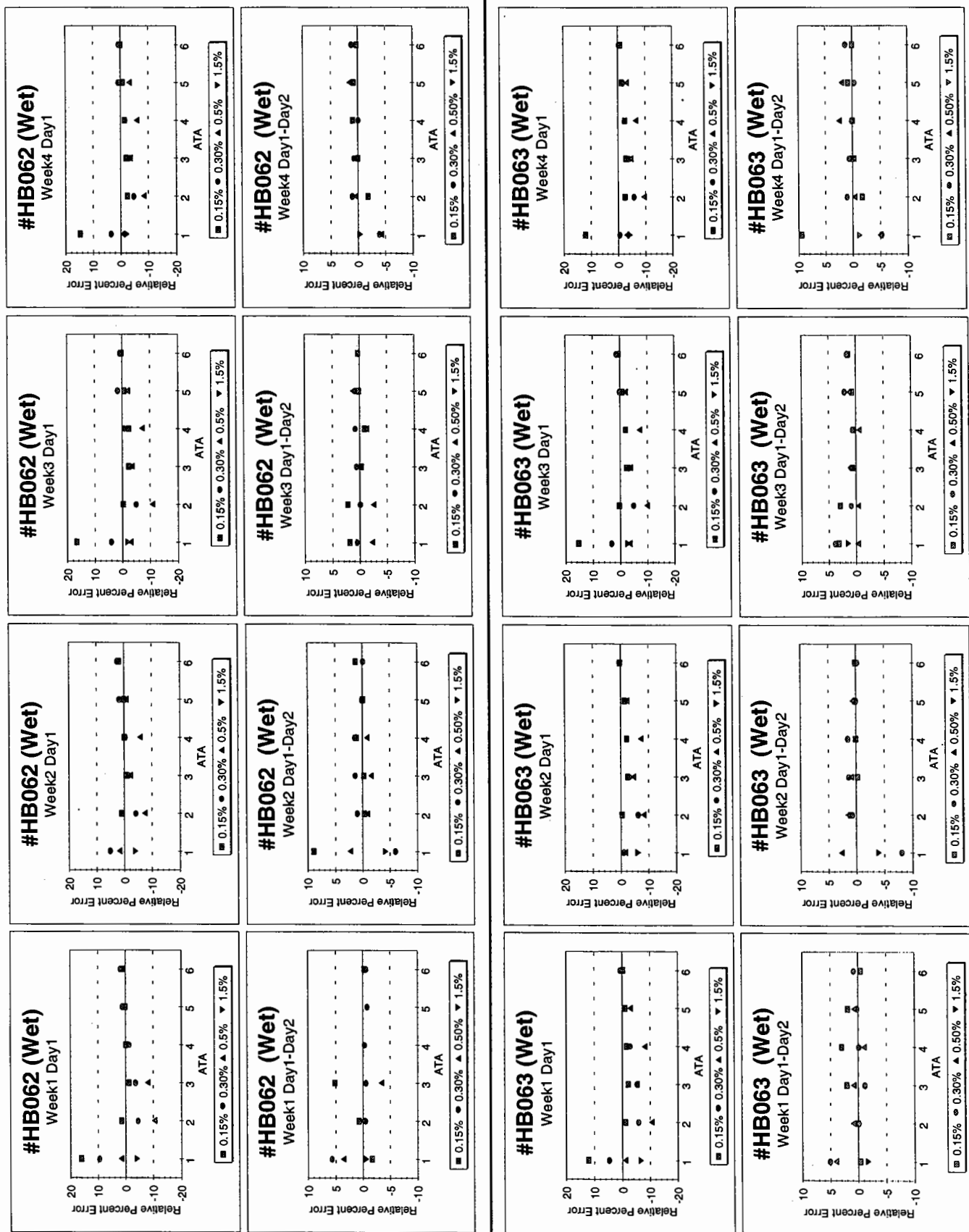


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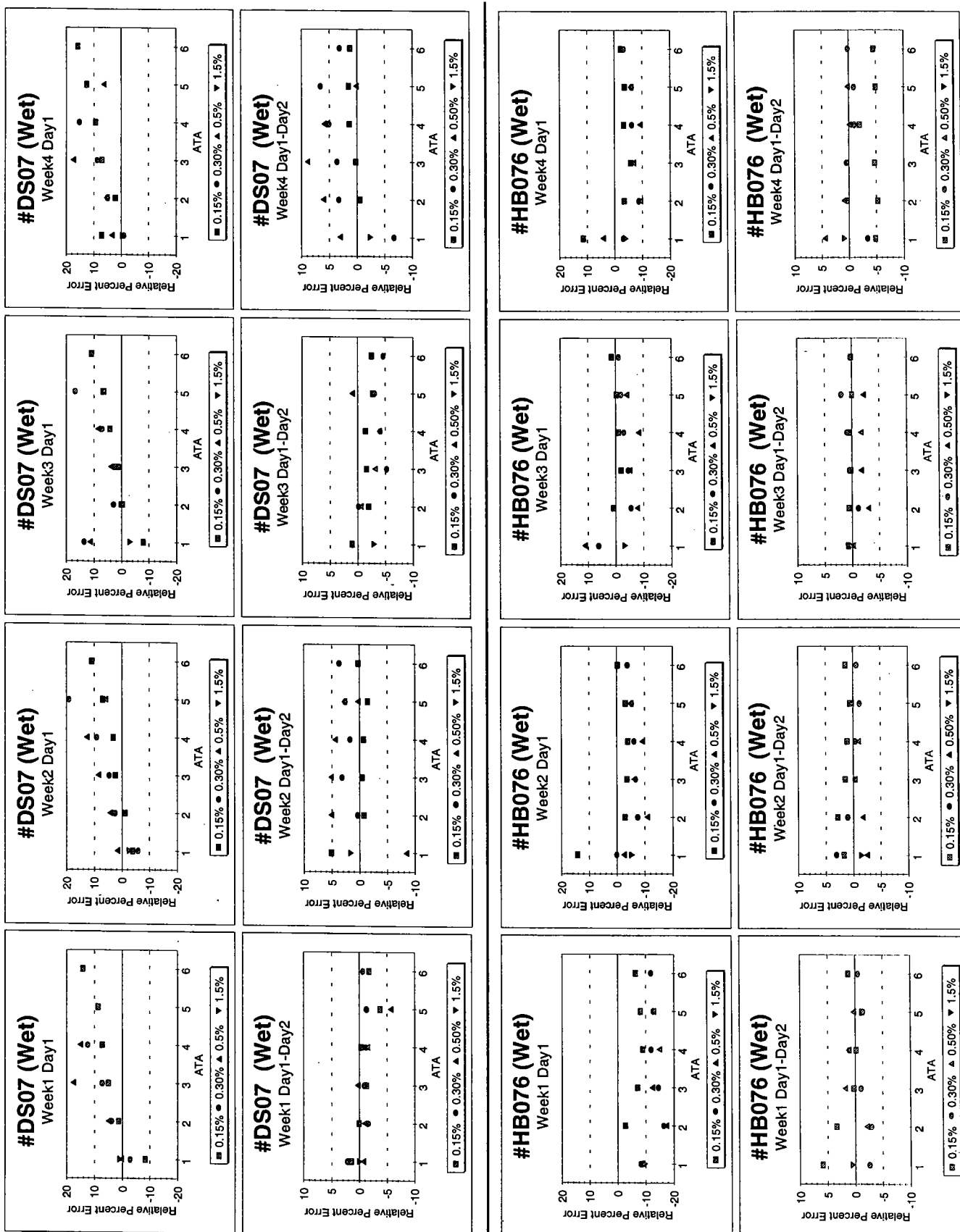


Figure 9. Effect of water vapor on hyperbaric accuracy - Field test units.

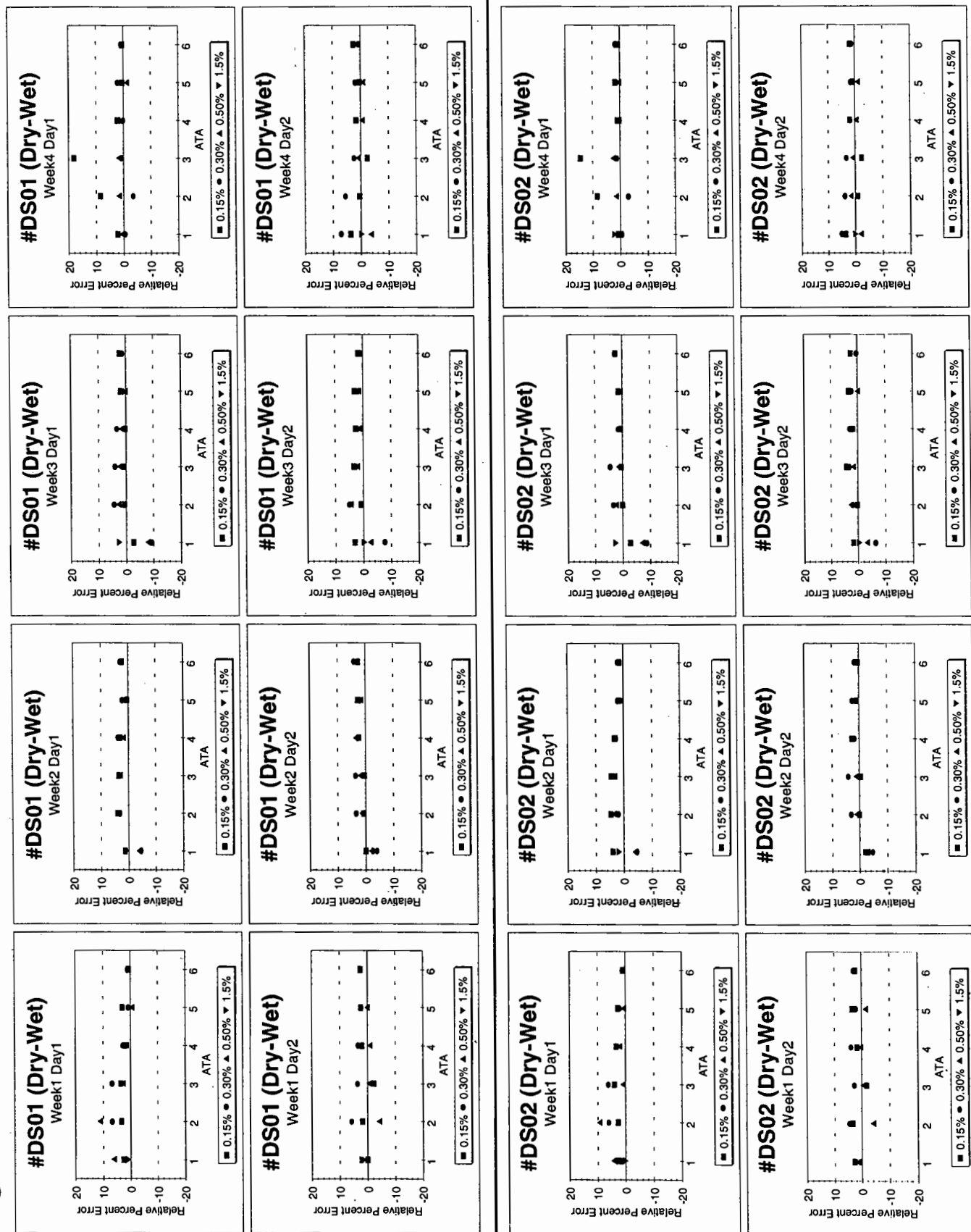


Figure 9. (cont.)

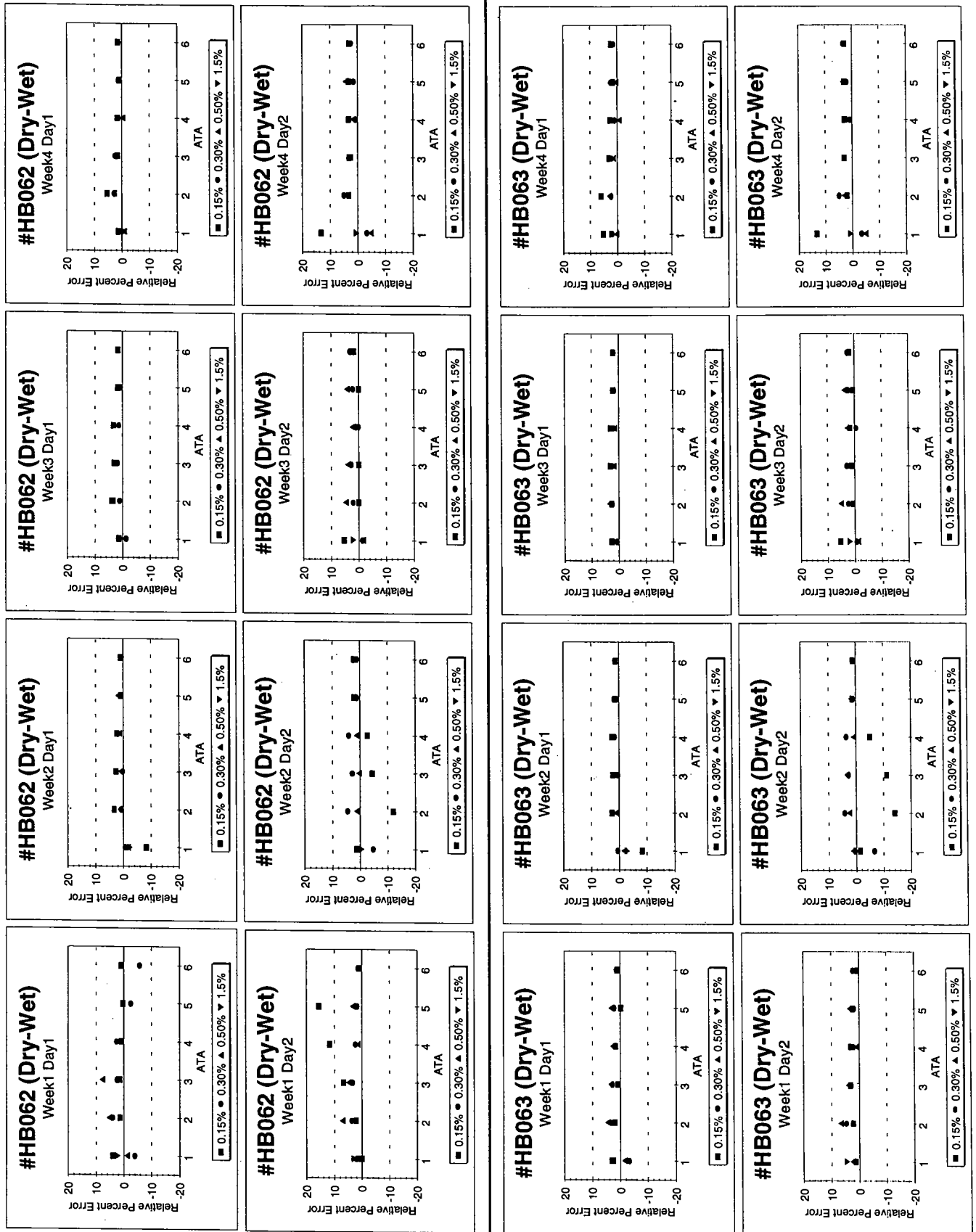


Figure 9. (cont.)

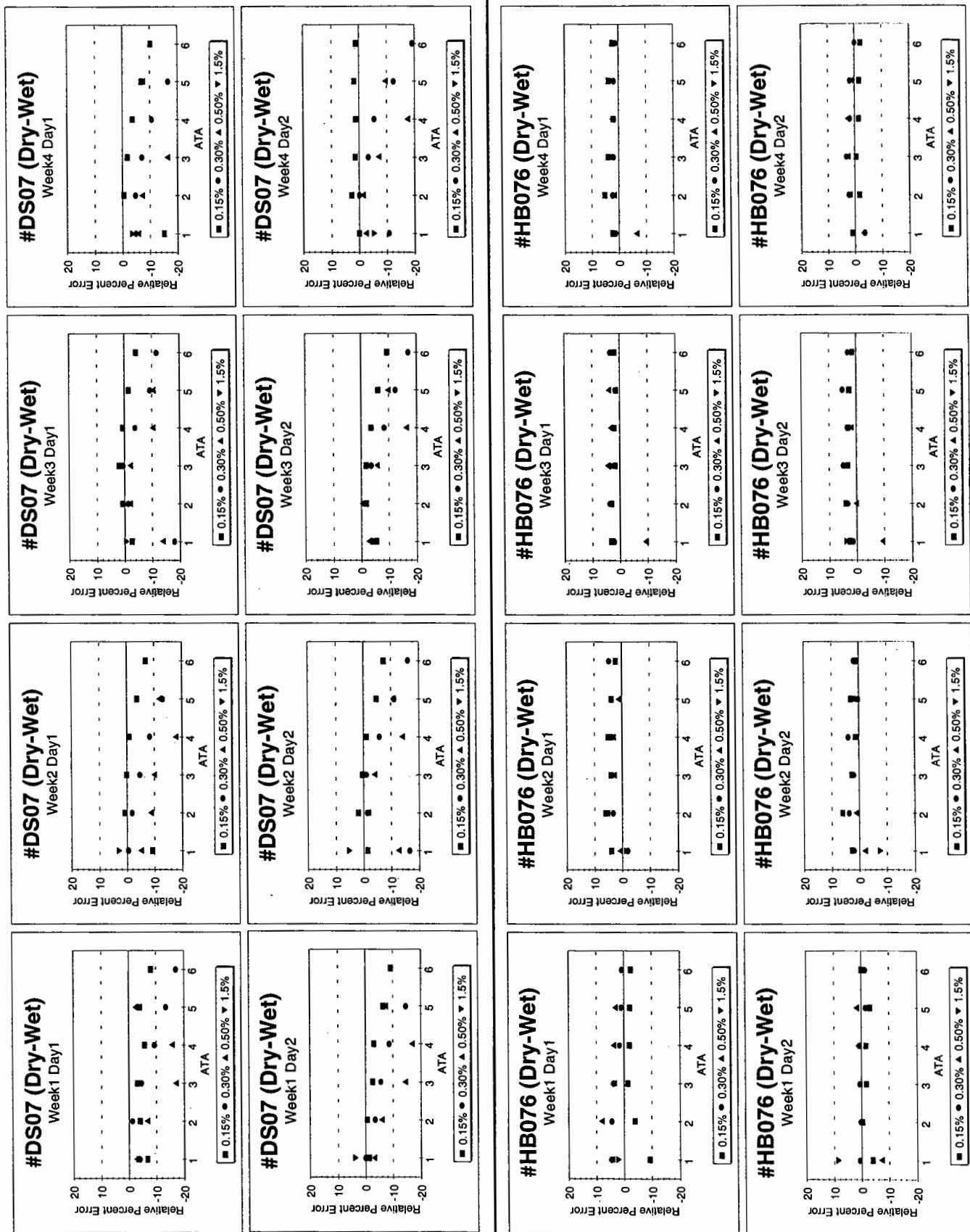


Figure 10. Hyperbaric accuracy - factory calibration - Fleet units.

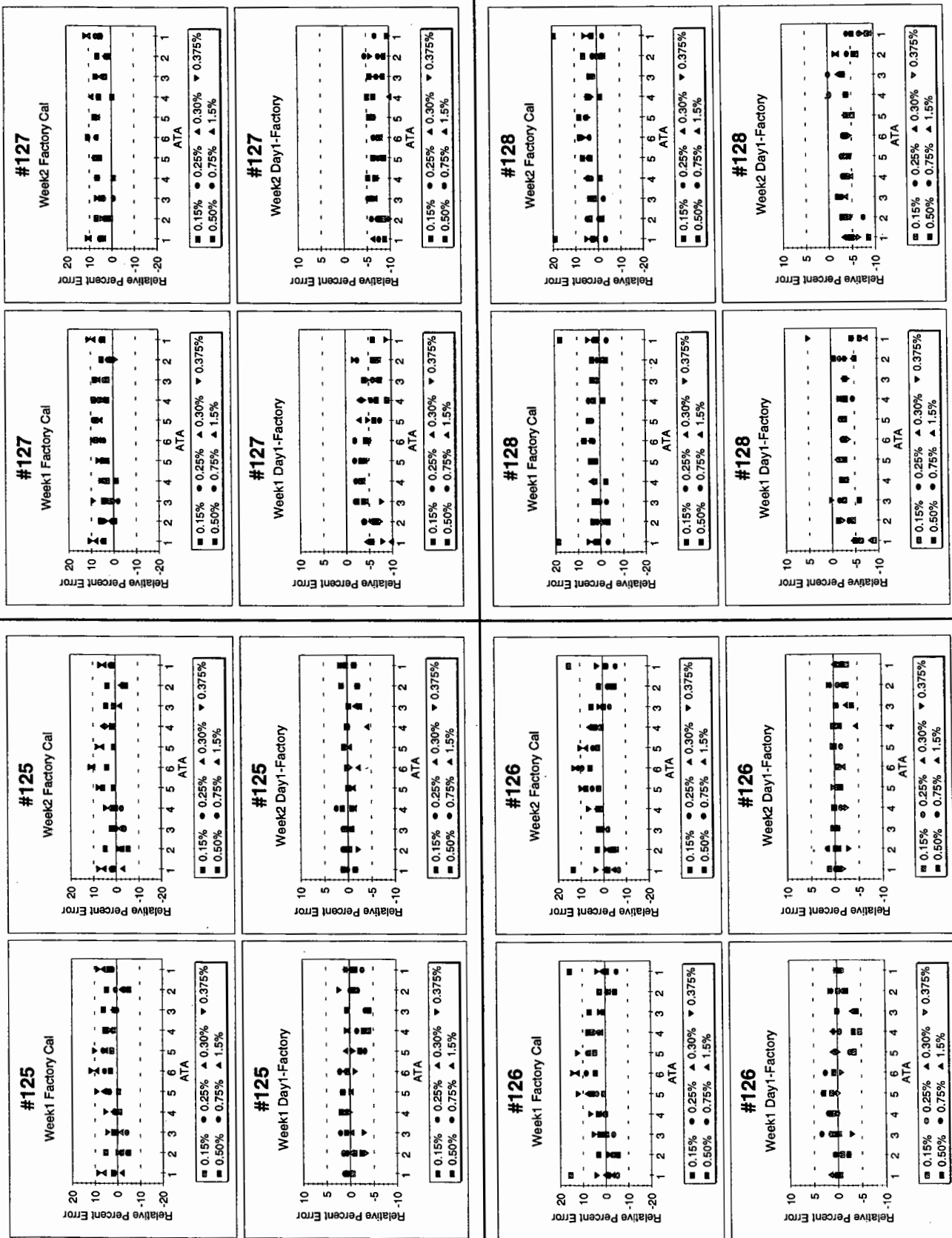


Figure 10. (cont.)

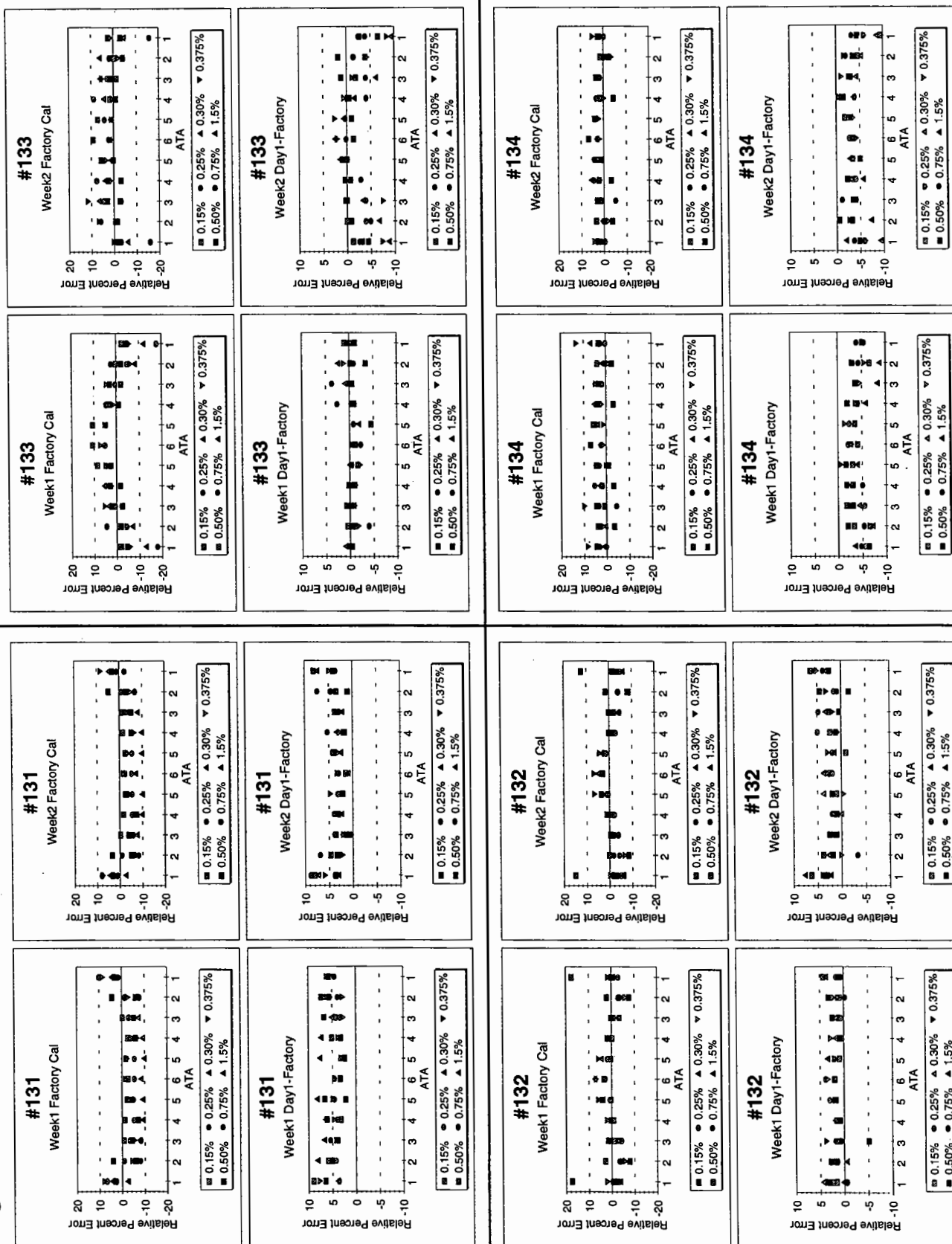


Figure 10. (cont.)

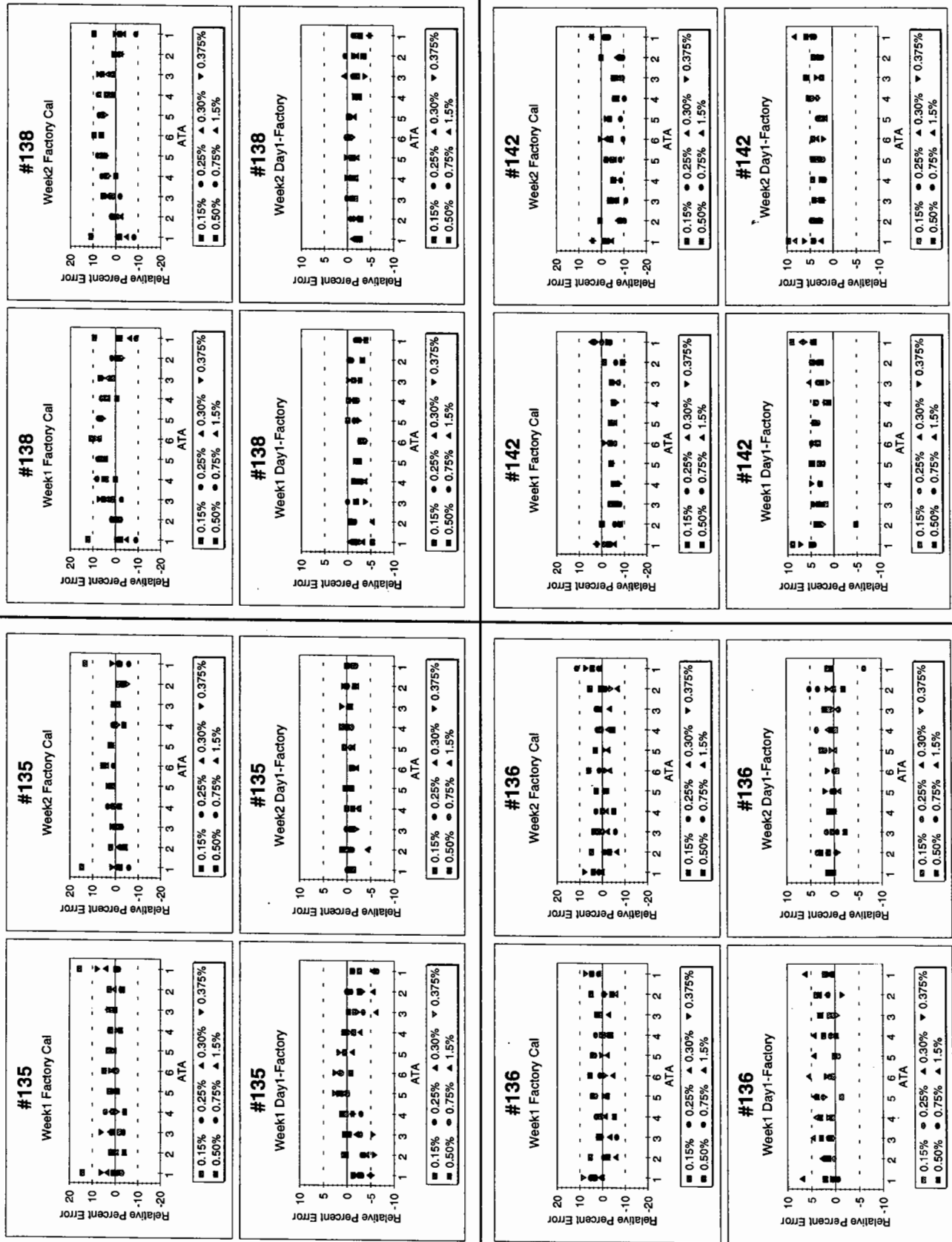


Figure 11. Response to temperature change - Field test units.

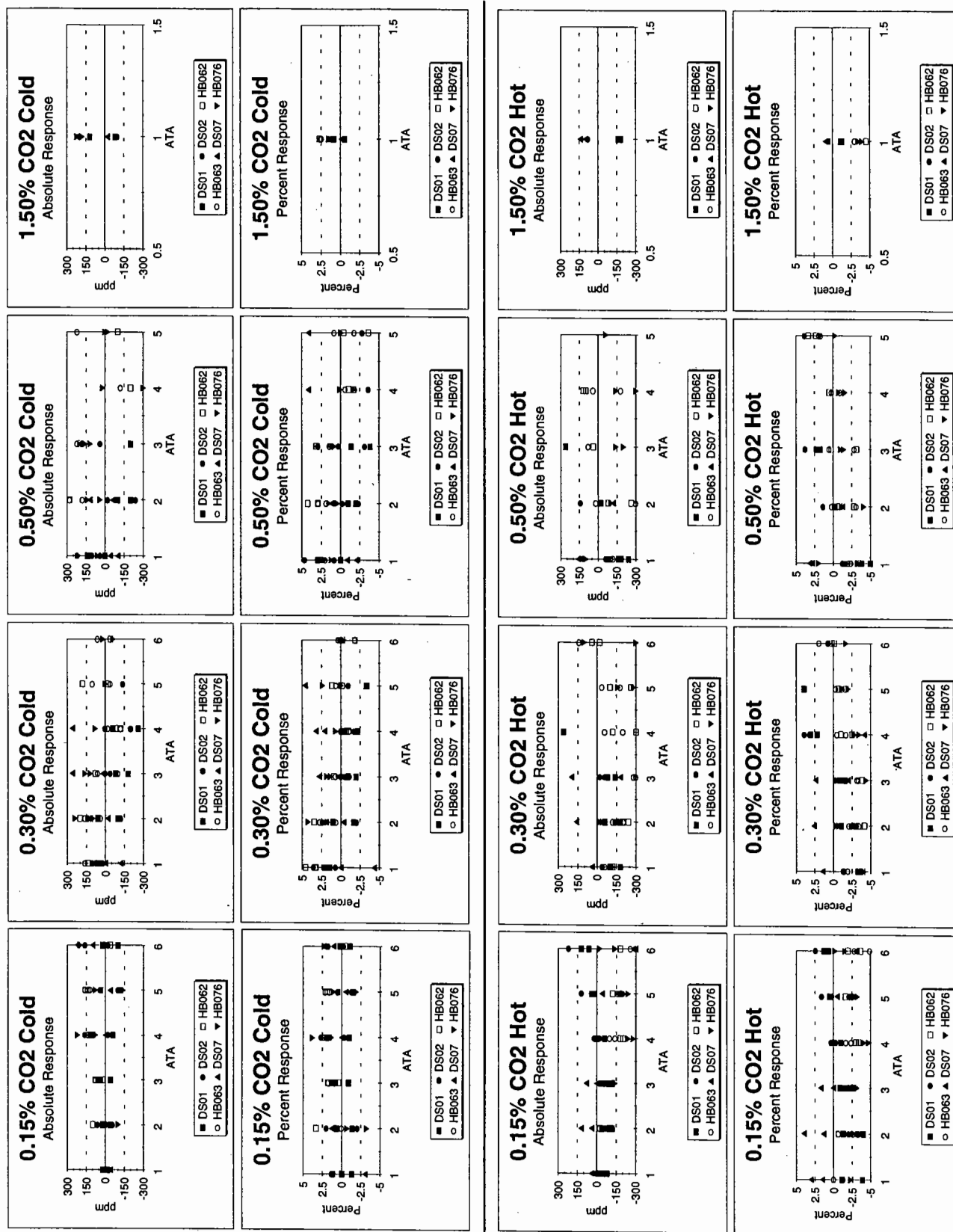


Figure 11. (cont.)

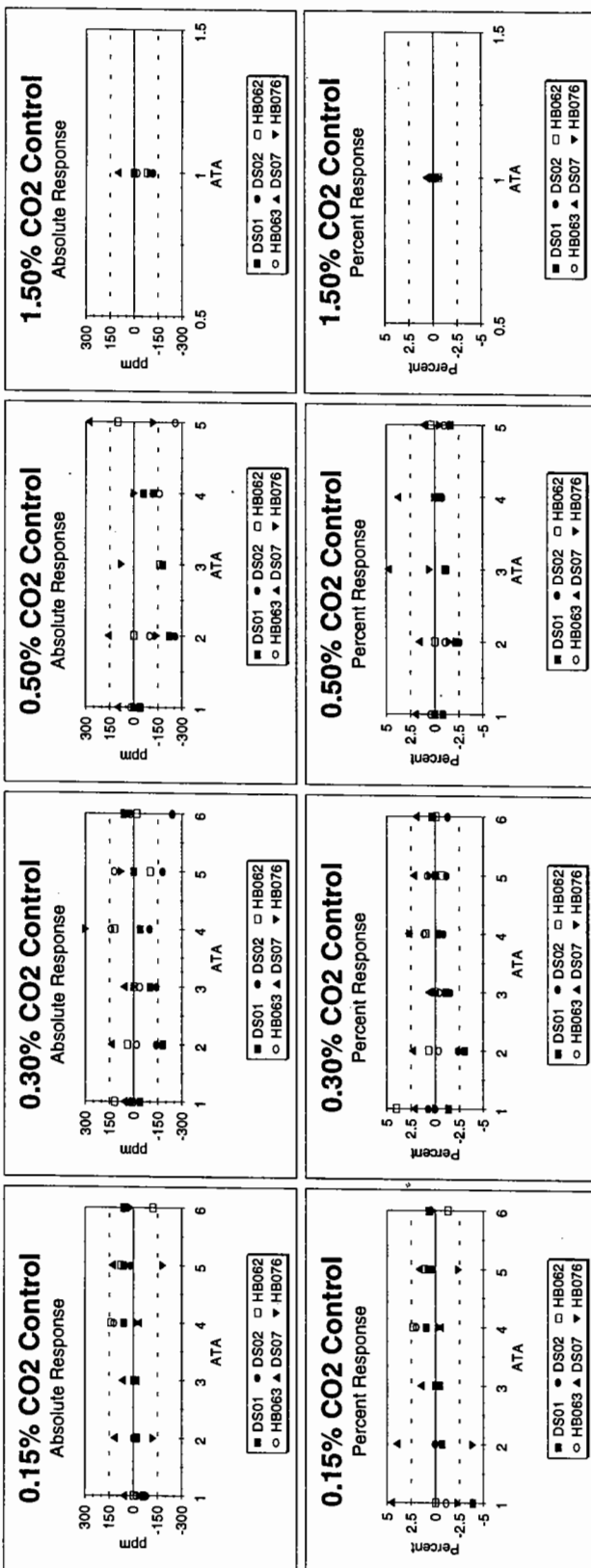


Figure 12. Recovery from temperature exposure - Field test units.

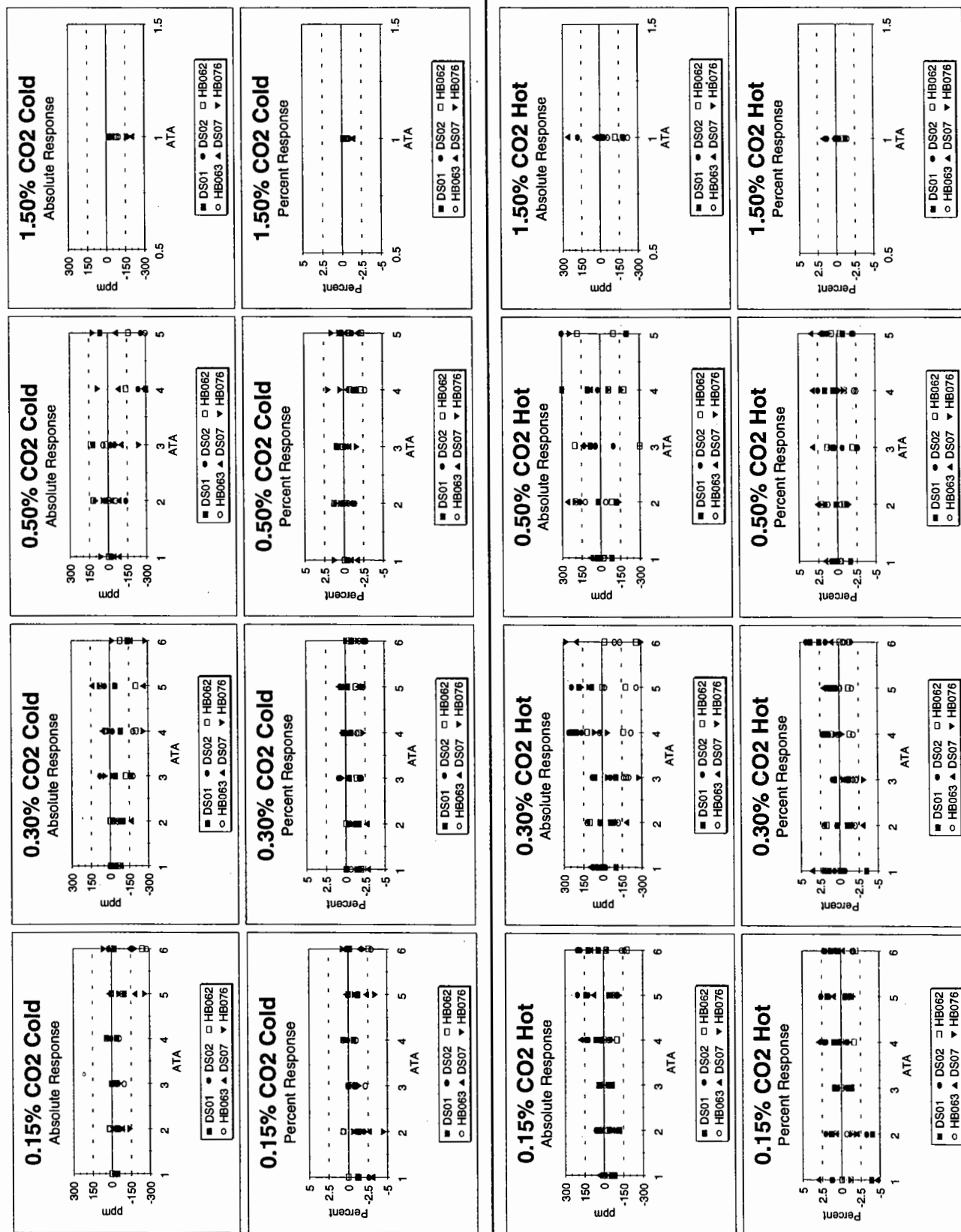


Figure 12. (cont.)

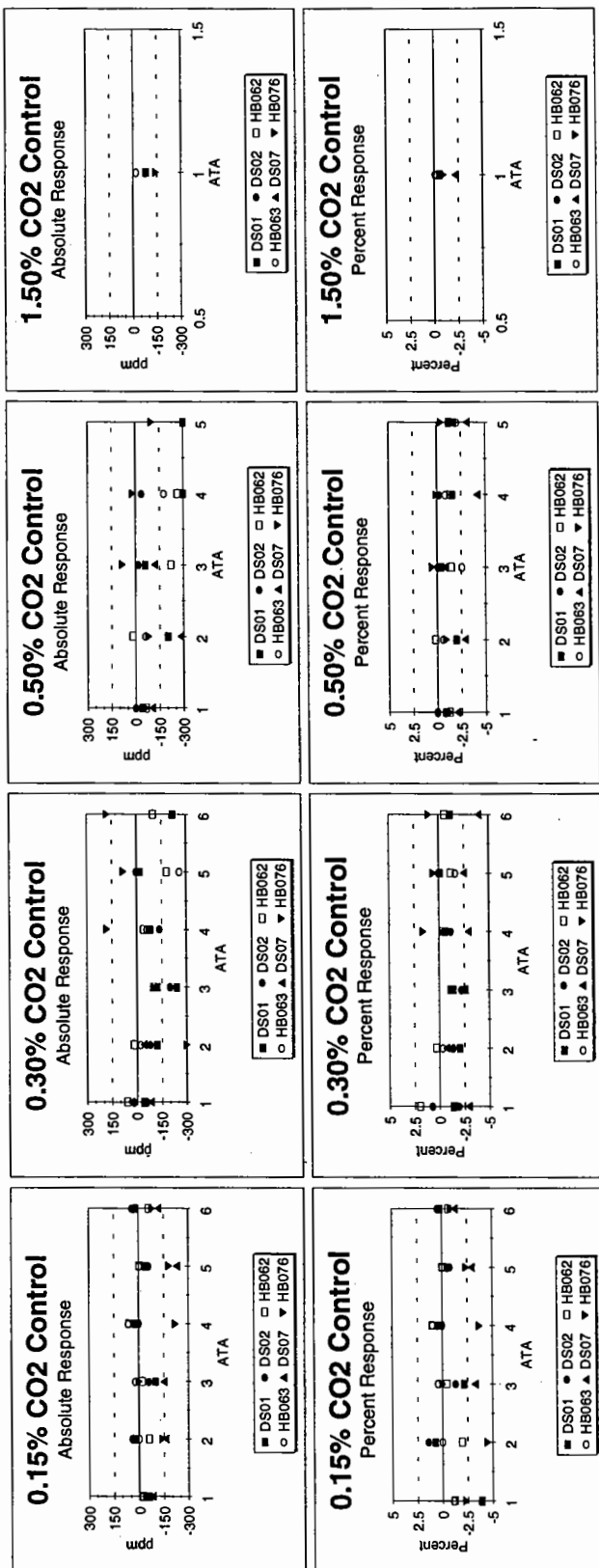


Figure 13. Hangar field test data.

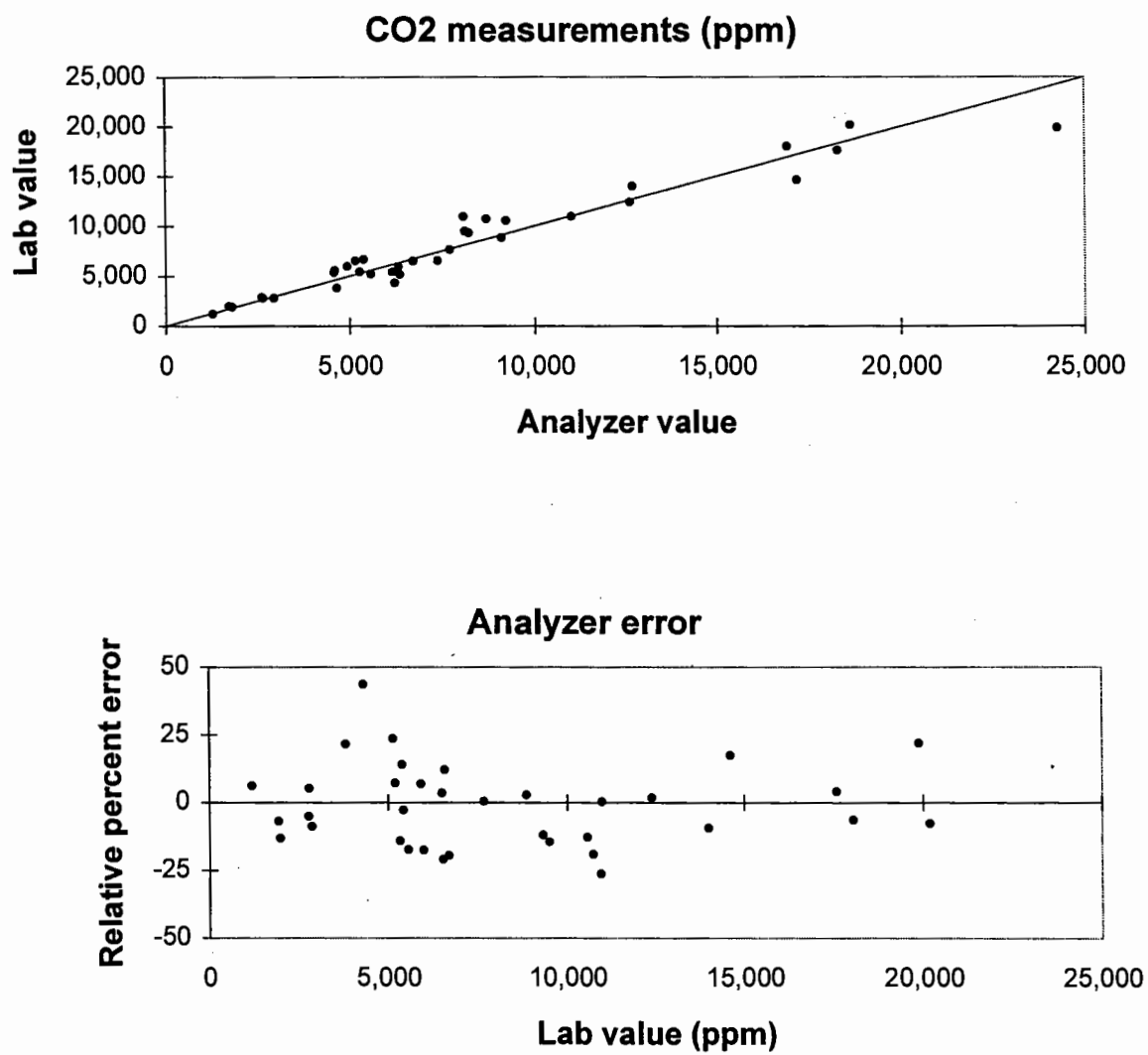


Figure 14. Trunk field test data.

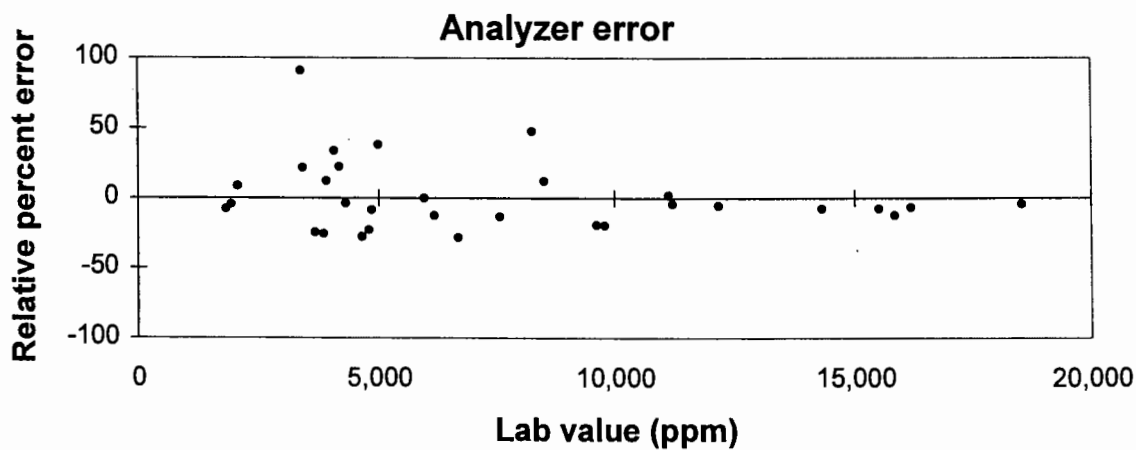
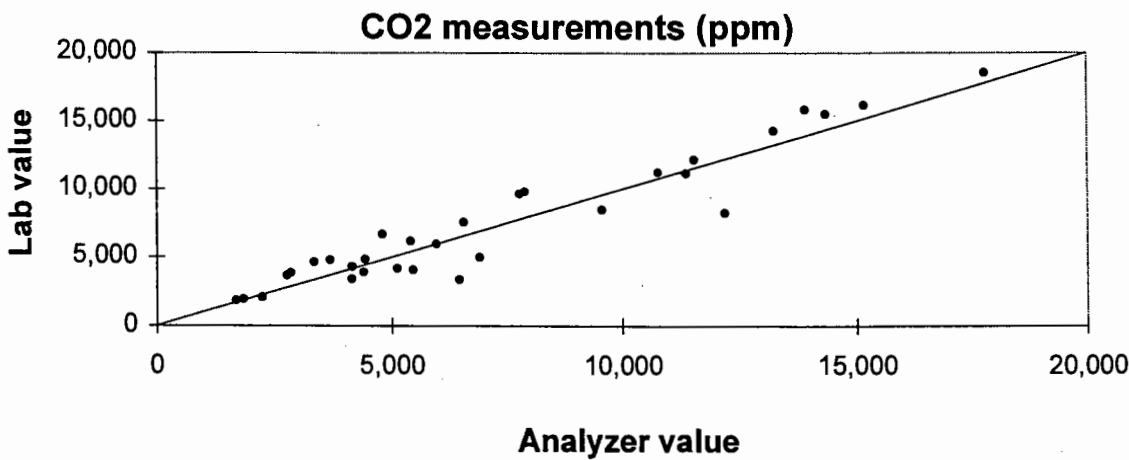
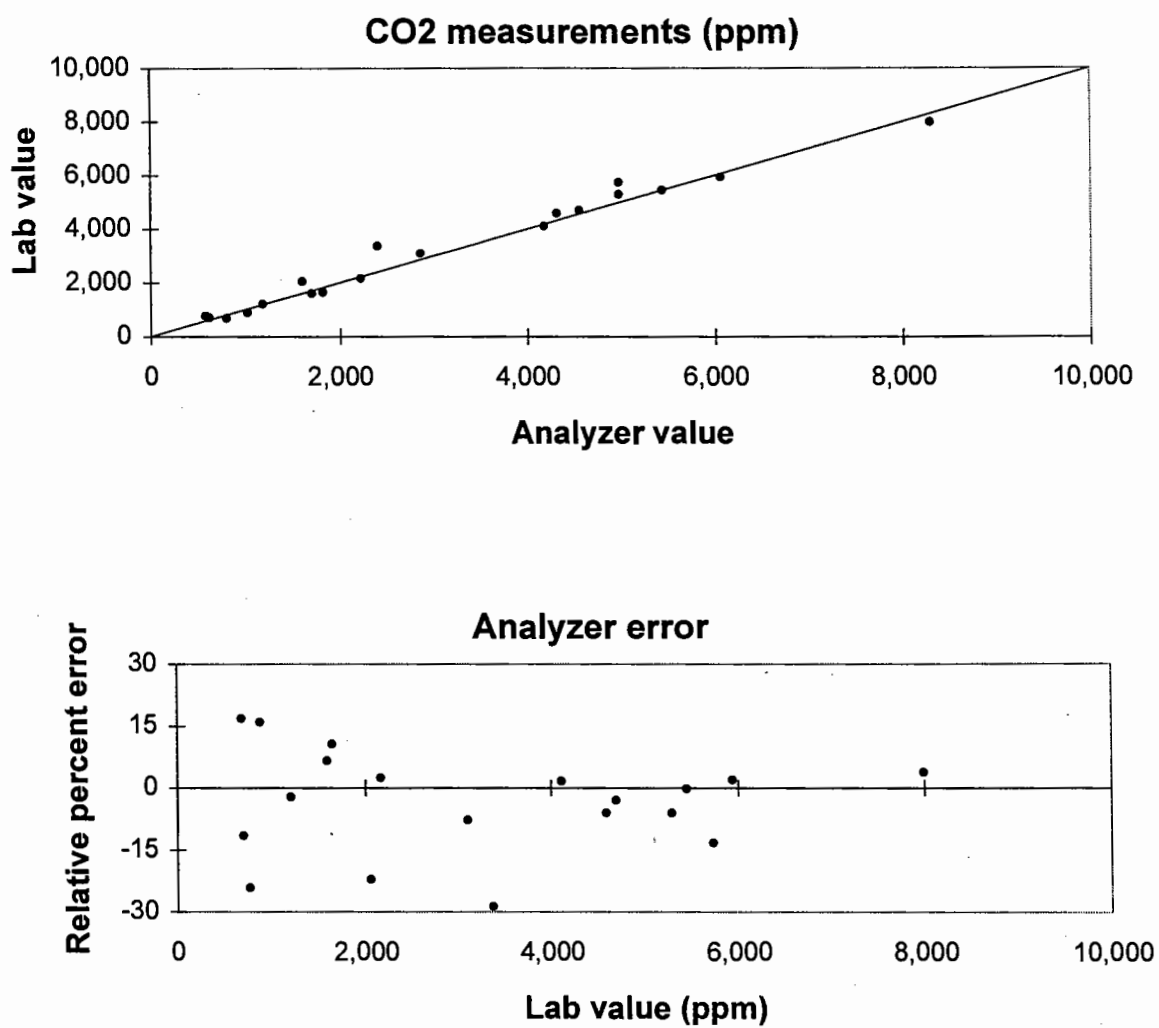


Figure 15. Chamber field test data.



APPENDIX A. FIELD TESTING PROTOCOL.

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FAX DSN 295-0782

Background

NMRI has been tasked by PMS-395 to develop a CO₂ monitoring system to help reduce the amount of air bank gas used to ventilate the DDS. Candidate CO₂ analyzers have been tested by NMRI and modifications made by the manufacturer in response to our needs. The current prototype analyzers have been approved for use inside DDS's for field testing only but have not been approved for regulating ventilation. This analyzer is the Geotechnical Infra-red Analyzer which measures CO₂ up to 2.5% sev at pressures up to 6 ATA. Field test results will help to evaluate:

- a. Stability and accuracy of instrument under actual field conditions.
- b. Effectiveness of current ventilation procedures.
- c. Draft operating procedures for the analyzer.

Test Summary

1. The bulk of testing will involve recording measurements made with the CO₂ analyzer during actual DDS operations. In addition, if opportunities arise, measurements may also be taken during ship's testing at dockside. Results will be used to estimate effectiveness of current ventilation procedures.
2. Analyzer calibration will be checked, and re-calibrated if necessary, on board using the CAMS-I calibration gas prior to each operation. Calibration data will demonstrate instrument stability under field conditions.

3. A limited number of gas samples will also be drawn, using NMRI cylinders, simultaneously when readings are being taken with the CO₂ analyzer. These gas samples will be analyzed later at NMRI to estimate the accuracy of the CO₂ analyzers under various conditions.

Test plan

1. Equipment

- a. 2 Geotechnical CO₂ analyzers for use up to 6 ATA
- b. Battery chargers for analyzers
- c. Sampling tubing
- d. Data sheets
- e. HP sample cylinders that have been evacuated

2. Check calibration (and re-calibrate if necessary) prior to use each day per Instrument Procedures (below). Record info on data sheet.

3. Check cylinder valves for tightness prior to going into the DDS. Do not use any cylinders that have loose valves and are suspected of having lost vacuum.

4. Take analyzer, cylinders, and data sheets into the DDS. Instrument is operated per Instrument Procedures (below).

5. Wait at least 40 s in one location before reading CO₂. Avoid breathing near the inlet of the analyzer when taking measurements as exhaled CO₂ will affect reading. Record info on data sheet. Subsequent readings should be taken at intervals no shorter than every 2 min.

6. Initial measurements can be made prior to closing of trunk hatch and beginning of ventilation.

7. Once the trunk hatch has been closed and ventilation cycles begun, record CO₂ measurements when feasible. These measurements should be taken when the test location (i.e., trunk, chamber, hangar and hangar bubble) is not being ventilated and after analyzer has stabilized. The most appropriate time will be immediately before each ventilation cycle.

8. An attempt should be made to take measurements in the 3 compartments at various times and depths with various number of personnel performing at different workloads.

9. For a few measurements, gas samples should simultaneously be taken in the exact location as analyzer measurements, using NMRI cylinders for later analysis at NMRI. Again, check cylinder valves for tightness just prior to use; do not use any cylinders that have loose valves and are suspected of having lost vacuum. Open the valve on one end of the cylinder:

a. Black handle valves (standard valves) should be opened completely.

b. Green handle valves (bellows valves) should be opened ~1 full turn until the tension on the handle is released; if the handle is turned much beyond that point, the handle will fall off and will have to be screwed back on.

After the cylinder valve has been opened, wait 30 s for equilibration of pressure and then close valve. Avoid breathing near the inlet of the analyzer or near the cylinder during sampling.

10. Record info on data sheet including cylinder # in rightmost column.

11. Use only 1 cylinder for each test; no duplicates will be taken here.

12. When convenient, input air to the DDS should also be measured with the CO₂ analyzer at SHA-162 (SSN 640 class) or SHA-94 (SSN 637 class). This can be facilitated if a low gas flow can be left on at SHA-162 or SHA-94 during operations. If this can't be done, purge at a highly audible flow rate at the sample site at least 5 min prior to CO₂ measurement. Before connecting instrument, turn down flow to just audible so that analyzer will not be overpressurized. Use calibration tubing with tee to connect analyzer to the point where gas is normally sampled for DDS air screening. These measurements may coincide with the current requirement of CO₂ analysis every 30 min during an operation. Remember that these portable CO₂ analyzer are not approved at this time for checking the CO₂ in the supply gas and you should rely on your present methods (i.e., detector tubes or CAMS-I) for this purpose.

13. For all measurements and cylinder samples, the data sheets should be filled out completely.

14. Check all cylinder valves for tightness just prior to loading into suitcase.

Instrument procedures

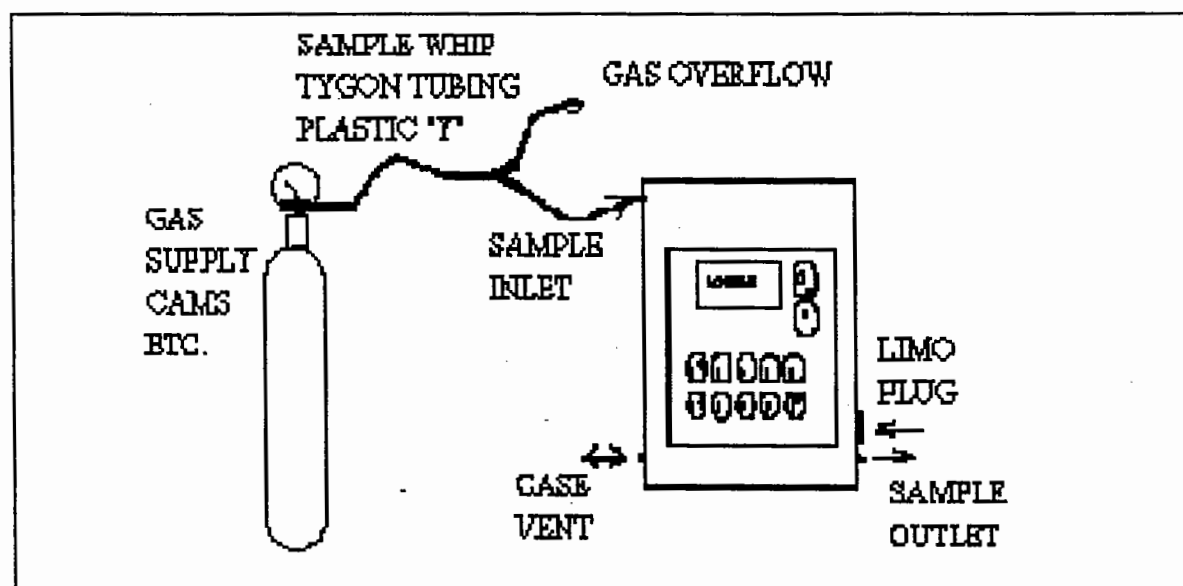
1. Batteries/charging

The CO₂ analyzer is run off its self-contained NiCad batteries. When the batteries require charging, the analyzer is attached to the charger that plugs into 110-volt line current outside of the DDS. Ideally, NiCad batteries should be fully discharged and recharged during use rather than continually topped off without a full discharge. However, this probably will not be possible

and the best approach is to check the battery well before an operation to allow time for overnight charging if the battery is low. Overnight charging should provide ~12 hours of usage. Note: the instrument must have batteries in place to operate.

Calibration check and re-calibration (if necessary).

1. A calibration check needs to be done once prior to each day's use.



2. Locate the CAMS-I calibration gas and insure that regulator is in place. Purge the CAMS-I regulator 3 times to insure removal of all ambient air from the regulator; then dial in a delivery pressure of several psig. Leave gas cylinder turned on but secure flow using the regulator outflow valve.
3. Install on the regulator the tubing that we have supplied. This tubing contains a tee to allow sampling with the analyzer. Connect the inlet port of the CO₂ analyzer to the side branch of tubing so that calibration gas can be sampled without pressurizing the analyzer.
4. Turn on analyzer by pressing the red key. The LCD will show the company name, model no., and information on key functions.
5. Press the "0" key to exit that screen. The LCD display will show the following choices:

1-General Utilities

- 2-Read Gas Levels
- 3-View/Print/Analyze
- 4-Download Data

6. Press "1" for General Utilities. The display will show the following:

- 1-Check Time/Date
- 2-Battery Status
- 3-Memory
- 9-More 0-Exit

7. Press "2" to read the available battery capacity. If there is insufficient charge, the analyzer will have to be charged.

8. Press "0" twice and then "2" twice to read gas level. Press "5" to turn on pump. Analyzer is now measuring CO₂. Allow to warm up for 5 min.

9. Open the CAMS-I regulator valve and adjust gas flow so it is just audible as it exits the tubing.

10. Wait at least 1 min for reading to stabilize. Analyzer display is in ppm CO₂ sev. Record reading at top of daily data sheet.

11. If reading is within 400 ppm of the calibration gas (e.g., $13,000 \pm 400 \text{ ppm} = 1.3\% \pm 0.0400\%$), calibration is unnecessary: go to step #16.

12. If calibration is necessary, press "0" to exit screen, "1" (General Utilities), "9" (More), "4" (Calibration), "1" (CO₂), "5" (Pump On), "1" (Calibrate).

13. Enter CO₂ concentration (e.g., 13,000 ppm = 1.3%). To backspace over an entry mistake, press and hold "0".

14. Press "0" to exit screen and then "1" (Yes) to calibrate.

15. Observe readout. Meter reading should be within 400 ppm of the calibration value. Calibration can be repeated if desired.

16. Shut off gas flow, close valve on CAMS-I cylinder, and bleed regulator down. Turn off analyzer by pressing red key. Remove tubing from analyzer.

17. The analyzer is ready to be taken into the DDS.

18. To begin measuring CO₂, simply turn on the instrument by pressing the red key, press "0", then "2" twice (Read Gas Levels), then "5" (Pump On); allow to warm up 5 min before using.

19. During the DDS operation, the analyzer can be turned off during periods of non-use, and turned back on and allowed to warm up 5 min before measuring CO₂.

CO₂ Analyzer Test Data Sheet
(Use New Sheet Each Day)

Analyzer Serial#: _____
 Cal Gas % CO₂: _____ %
 Cal Gas Cylinder#: _____
 Cal Gas Reading: _____ %
 Time checked: _____
 Re-calibrated: Yes ___ No ___

Date: _____
 Submarine: _____
 Person doing testing: _____
 SPHERE: _____

Time	Pressure (fsw)	Depth of Water in Sphere (fsw)	Time of EVERY Vent	# of Divers	Diver Activity	CO ₂ (ppm) ANALYZER READING	Cylinder# (If take sample)

Notes:

APPENDIX B. OPERATING PROCEDURES FOR THE HYPERBARIC CO₂ ANALYZER.

Sufficient information is provided here to calibrate and measure CO₂ during DDS operations onboard a submarine. It is assumed that the calibration gases will be brought onboard by the SDV personnel. However, the ship's CAMS-I calibration gas (1.2-1.5% CO₂) can be used as a backup if the normal CO₂ runs out.

Batteries/Charging

The CO₂ analyzer is run off its self-contained NiCad batteries. When the batteries require charging, the analyzer is attached to the charger, which plugs into 110-volt line current outside of the DDS. Ideally, NiCad batteries should be fully discharged and recharged during use rather than continually topped off without a full discharge. However, this probably will not be possible and the best approach is to check the battery well before an operation (described below) to allow time for 24 h charging if the battery is low. Complete recharging should provide ~12 h of usage. Note: the instrument must have batteries in place to operate.

Calibration gas and equipment

Two charged high-pressure cylinders (one as a spare) of calibration gas containing ~15,000 ppm (~1.5%) CO₂ in hydrocarbon-free air (primary gravimetric standard with accuracy guaranteed to ±1% relative) are needed. Cylinders should preferably contain at least 30 ft³ of gas to insure an adequate volume of gas for repeated calibrations. One high-purity regulator (with stainless steel diaphragm, 0-50 psi delivery pressure) with an appropriate CGA fitting will be needed to install onto the cylinders. Gas mixtures and regulators can be obtained from: 1) Scott Specialty Gases, Plumsteadville, PA; 2) Air Products and Chemicals, Inc., Allentown, PA; or 3) MG Industries, Specialty Gas Division, Malvern, PA; as well as from other suppliers.

Tygon or rubber tubing (~3/16 inch inner diameter) and hard plastic tees are used to construct the calibration tubing as shown below.

Battery/Calibration check and re-calibration (if necessary)

1. A battery/calibration check needs to be done once prior to each day's (operation) use.
2. Locate the calibration gas and install the regulator if not already in place. Purge the regulator 3 times to insure removal of all ambient air from the regulator; then dial in a delivery pressure of several psig. Leave gas cylinder turned on but secure flow using the regulator outflow valve.
3. Disconnect analyzer from charger.

4. Turn on analyzer by pressing the red key. The LCD will show the company name, model no., and information on key functions.

5. Press the "0" key to exit that screen. The LCD display will show the following choices:

- 1-General Utilities
- 2-Read Gas Levels
- 3-View/Print/Analyze
- 4-Download Data

6. Press "1" for General Utilities. The display will show the following:

- 1-Check Time/Date
- 2-Battery Status
- 3-Memory
- 9-More 0-Exit

7. Battery check. Batteries should be checked without the charger connected. Press "2" to read the available battery capacity. If there is insufficient charge (< 50%), the analyzer should be charged.

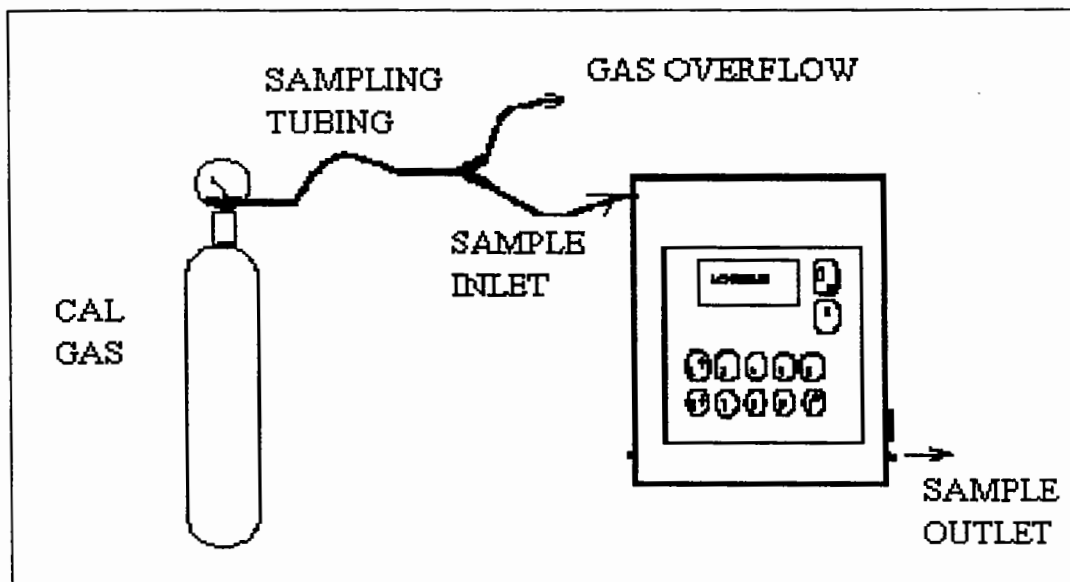
8. Install on the calibration regulator a short (< 1 ft) length of Tygon or rubber tubing that contains a tee with a side branch of ~6 in. Connect the inlet port of the CO₂ analyzer to the side branch of tubing so that calibration gas can be sampled without pressurizing the analyzer.

9. Press "0" twice and then "2" twice to read gas level. Press "5" to turn on pump. Analyzer is now measuring CO₂. Allow to warm up for 5 min.

10. Open the calibration regulator valve and adjust gas flow so it is just audible as it exits the overflow.

11. Wait at least 1 min for reading to stabilize. Analyzer display is in ppm CO₂ sev.

12. If reading is within 400 ppm of the calibration gas (e.g., $15,000 \pm 400 \text{ ppm} = 1.5\% \pm 0.0400\%$), calibration is unnecessary: go to step #17.



13. If calibration is necessary, press "0" to exit screen, "1" (General Utilities), "9" (More), "4" (Calibration), "1" (CO₂), "5" (Pump On), "1" (Calibrate).

14. Enter CO₂ concentration (e.g., 15,000 ppm = 1.5%). To backspace over an entry mistake, press and hold "0".

15. Press "0" to exit screen and then "1" (Yes) to calibrate.

16. Observe readout. Meter reading should be within 400 ppm of the calibration value. Calibration can be repeated if needed.

17. Shut off gas flow, close valve on the cylinder, and bleed regulator down. Turn off analyzer by pressing red key to conserve batteries. Remove tubing from analyzer.

18. The analyzer is ready to be taken into the DDS.

Use during DDS operations

1. To begin measuring CO₂, simply turn on the instrument by pressing the red key, press "0", then "2" twice (Read Gas Levels), then "5" (Pump On); allow to warm up 5 min before using.

2. The accuracy of the pressure reading shown on the analyzer's display is unknown.
3. During the DDS operation, the analyzer can be turned off during periods of non-use by pressing the red key, and turned back on and allowed to warm up 5 min before measuring CO₂.

If dropped in the water

1. If the analyzer is dropped into the water, it will float. If the pump is operating, water can be drawn into the inlet filter located on one side of the case and flow will stop. A flow sensor inside the analyzer will then detect the absence of gas flow and turn the pump off within several seconds.
2. To put the analyzer back into operation, the filter is first removed by unscrewing the retaining nut and gently pulling it out by the fingers. The filter then can be replaced or simply blown out by mouth or with a gentle flow of gas.
3. Normal startup procedure is then followed.

Cold start (when there is a suspected problem)

1. When there is a suspected problem with the analyzer, the cold start option reboots the software and often restores the analyzer to normal operation. Problems often cured with a cold start include: 1) analyzer not responsive to key strokes and 2) analyzer display indicates that it will not accept the calibration value that is entered.
2. Cold start procedure:
 - a. Hold the "3" key and turn the analyzer on by pressing the red key.
 - b. The display should show "Cold Start". Press "1" to continue.
 - c. After a cold start, the alarm values must be re-entered or the analyzer will beep and show "max" on the display.
 - d. Press "0" to exit from the information display, "1" (General Utilities), "9" (More), and "5" (Alarm Levels).
 - e. Press "2" (Max) and "1" (CO₂)
 - f. Enter a value of 26,000 ppm (or other selected concentration), then press "0" 3 times to return to the main menu.

Factory calibration (when calibration gas is unavailable or suspect)

1. When no calibration gas is available or a problem with the gas on hand is suspected, the analyzer can be reset to the default factory calibration.

2. Reset to factory calibration procedure:

- a. Turn the analyzer on by pressing the red key.
- b. Press "0" to exit from the information display, "1" (General Utilities), "9" (More), "4" (Calibration), and "5" (Factory Settings).
- c. Press "1" (Yes) when prompted: "CAUTION Returning to factory setting of calibration and zero?"
- d. Press "0" twice to return to the main menu.

Factory repair/Maintenance service

1. Analyzers are kept under service contract with the manufacturer (Geotechnical Instruments). This contract needs to be renewed annually (at the start of every fiscal year).

2. This service contract provides for the following:

- a. One planned yearly service by the manufacturer that includes re-calibration, battery replacement if needed, any necessary repairs, and general checkout of instrument function.
- b. Free software upgrades.
- c. Hardware modifications due to product improvement providing the modification is compatible with the current unit: no extra charge.
- d. Repair of any malfunction in the field: no extra charge. This excludes excessive physical damage.
- e. Shipping charges to and from Geotechnical Instruments, U.K. and the SDV sites. Shipping labels will be provided by Geotechnical Instruments.

3. In the event of a problem with an analyzer that cannot be corrected by the above suggested steps, contact the manufacturer via telephone. In the U.S., dial "011-44-1926338111". Outside of the U.S. dial: commercial +44(0)1926 338111.